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ARTIFICIAL SILK

A COMPLETE TREATISE ON
THE THEORY, MANUFACTURE AND MANIPULATION
OF ALL THE KNOWN TYPES OF ARTIFICIAL SILK

BY

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Translated from the German by

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WITH 96 ILLUSTRATIONS

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INTRODUCTION

In spite of its name, which is only partially justified, artificial silk cannot be considered as a complete substitute for natural silk. It must, on the contrary, be looked upon as an independent textile fibre of peculiar character, which has to a large extent special applications and fields of use. It has also, in the course of years, acquired a footing in a number of fields of application, which were, until about ten years ago, exclusively dominated by the natural product.

It should be remembered that in regard to its production and properties the artificial product has much in common with the natural fibre. From the physical standpoint the spinning processes by which both fibres are produced are completely analogous. For these reasons it appears suitable that before considering artificial silk we should briefly describe the origin, manufacture, and properties of the natural product.

True silk, the most valuable textile fibre, is the fibrous product within which the larva of the Mulberry Silk-worm Moth (*Bombyx mori*) envelopes itself by spinning, before transformation into the chrysalis. This moth is reared for silk production partly in large, well-equipped magnaneries, but also largely as a cottage industry.

The moth has a breadth of about 5 cm. (2 in.) with outstretched wings and is about 2 cm. (0·8 in.) long. The wings are of a dirty white colour, with two or three darker cross bands and a more or less definite brownish half-moon on each forewing. The male usually dies soon after mating and the female soon after laying, the number of eggs being ordinarily 200 to 300. The eggs are of about the size of poppy seed and have at first a greyish yellow colour which turns later to a greyish blue.

The eggs are kept in cool, dark store-rooms, in a carefully dried condition, until the commencement of the breeding season. In the spring they are transferred to light and well-aired

hatching rooms where they are exposed to a rising temperature of 10 to 25° C., whilst spread out on sheets of paper or other material, until the larvae are hatched, in about two weeks. These are then fed with mulberry leaves on frames until, after changing their skin from four to six times, and in about a month, they are fully grown and cease to feed. They are then about 10 cm. (4 in.) long, weigh about 5 gm. (0·18 oz.), and are smooth, of a lustrous whitish colour, with various grey and reddish spots and a horn on the last segment. They are now placed on twigs or straw in the spinning huts where they immediately commence to spin the cocoons.

Spinning lasts about four days, and takes place as follows: The silk-worm squirts a viscid excretion, fibroin, from two lateral spinning glands, lying under the mouth, attaches the small drop which is first formed to any point of its surroundings, and by peculiar backward movements of its head it then draws the liquid out to a fine thread, which solidifies immediately in the air, and which is attached, whilst still moist, to numerous points of the spinning hut. The two individual strands of the thread are enveloped by sericin, which is simultaneously exuded, by which means they are stuck together to form what is effectively a single thread. (After drying this sericin forms the so-called silk-gum, which is usually removed later, ordinarily before dyeing, by treatment with hot soap solution.)

In this manner, and with the help of its foremost feet, which assist in the spinning and winding processes, the silk-worm first forms an irregular, loose, and tangled mass of fibre, which is known as flock silk. Gradually, however, the silk-worm envelopes itself in very regular figure-of-eight loops, and so forms a dense, tight, uniform envelope, with a smooth internal wall, the cocoon proper. Cocoons containing a female chrysalis are contracted in the middle. The inner wall of the cocoon is also coated with sericin, and, after drying, this forms an inner, parchment-like membrane. It occasionally happens that two silk-worms spin a common cocoon. Such double cocoons are valueless, as the threads are hopelessly entangled.

The cocoons are next sorted, the useless ones removed and a number selected for breeding purposes. After killing the

chrysales by heat, those to be used for silk recovery are sorted into qualities. The best yield organzine, the medium quality tram silk, and the poorest single silk. In order to reel the silk, the cocoons are first thrown into hot water and vigorously stirred with suitably shaped brushes or similar contrivances. This causes the silk-gum to swell and the ends of the threads adhere to the brushes. A short length of thread is then unwound by hand, passed through the slots and guides of the reeling machine, and the rest of the silk is then unwound by the revolution of the latter. Several cocoons are always reeled simultaneously and the fibres united to a single thread, consisting of 3 to 30 individual fibres, according to the variety of silk to be obtained.

As, in the case of ordinary silk, these parallel individual threads are very long, true spinning, in the sense of the production of a long thread from relatively short fibres, is not required. The further treatment consists in reeling, twisting, doubling, and so forth, which are carried out by the usual methods of the textile industry. The case is otherwise for waste silk and schappe silk, which are produced from the above-mentioned tangled flock silk fibre and other silk waste, that is, from a material of relatively short fibre, which has first to be spun to a continuous long thread, in a manner similar to cotton or wool, usually after the silk-gum has been removed by degumming with alkalis or soap solution as in the case of reeled silk. For quite special purposes, such as the manufacture of bolting-cloth, linings, crape and so forth, raw silk is used without degumming, more particularly where the qualities of hardness and stiffness, peculiar to raw silk, are required. Sewing, knitting and crochet silk are almost always produced from silk which has not been degummed.

True silk forms a perfectly homogeneous, uniform thread of almost circular cross-section (see Fig. 1). The diameter of the thread is 0·01 to 0·02 mm., its specific gravity 1·25, its tensile strength 40 kg. per sq. mm., its breaking length 32·5 km. Silk is dissolved rapidly—within one minute—by both alkalis and hot hydrochloric acid solution. It consists chemically of 50 to 60 per cent of fibroin, which is nitrogenous, 24 to 25 per cent

of albumen, and small quantities of fats, waxes, resins and dyestuffs. The sericin of the silk-gum is probably an oxidation product of fibroin. Silk is relatively very hygroscopic, as it may absorb about 30 per cent of moisture from the atmosphere without any very recognizable change. Before being sold it is, therefore, dried in so-called conditioning establishments to a defini e degree of dryness and its true dry weight established. The usual " commercial weight " is the dry weight as determined at 110° C. + 11 per cent. Both silk and artificial silk are classified in terms of " deniers," which denote the weight

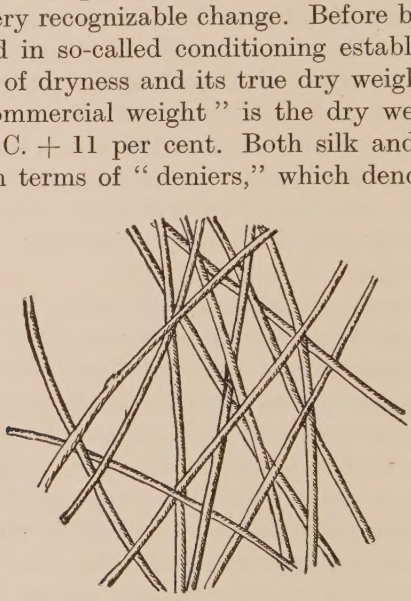

FIG. 1. NATURAL SILK. DEGUMMED
Magnification 80

in grammes of a thread 9000 metres long. As used for the manufacture of textiles, silk is usually weighted to an extraordinary extent by impregnation with, for example, tin oxide, tin phosphate or tin phosphosilicate. In this manner the weight of the silk is often increased two or threefold. The durability of the material is considerably reduced by weighting. In particular, the very heavily weighted, so-called sick silks are usually very sensitive to light and very liable to deterioration on storage.

Apart from true silk there are a whole series of " wild " silks produced by moths of other species. Of these the best known in Europe is Tussah silk, produced by the Chinese and Indian Tussah moths, the fibre of which is ribbon-shaped and from two

to three times as wide as true silk, also showing under the microscope a definite longitudinal striation and numerous points at which it is doubled over. We must also mention the Yamamay silk of the Japanese oak silk moth (*Antheraea Yamamay*), a moth producing a single thread and very closely related to *Bombyx mori*, for which reason Yamamay silk is fairly similar to true silk. Other wild silks are the Kurimushi silk of Japan, Korea, and China, and Anaphé silk of Africa, together with many others. The wild silks are rather less soluble than true silk in boiling hydrochloric acid solution, requiring two minutes for solution.

We may also mention, merely in passing, spider silk, which was produced from the spinning glands of spiders, more particularly of the large Madagascar species, *Nephila Madagascariensis*, by withdrawing the fibre artificially. These fibres almost equal true silk in tensile strength (38 kg. per sq. mm.), and breaking length (29·6 km.) and surpass it in extensibility, which is over 30 per cent. On the other hand, spider silk swells very considerably in water. The possible production is too small for technical use. Regarding the spider silk works of Cachot, in Paris, see *Wagners Jahresberichte*, Vol. 47, II, page 589.

The extraordinary strength of the true silk fibre, together with its delightful soft but brilliant lustre, its exceptional suitability for the weaving loom, and the wonderful feel of the fabrics produced from it, have caused silk to be the most valued raw material of the textile industry since the dawn of history. It is not surprising that the problem of producing such a material artificially was especially attractive to the untiring human intellect. It is quite possible that even before chemistry and technology were ripe for the solution of the problem it was dreamt of by more than one inventive genius. In the following section, which will deal with the historic development of the artificial silk industry, we will see how the dream came true.

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ARTIFICIAL SILK

GENERAL SECTION

CHAPTER I

THE HISTORICAL DEVELOPMENT OF THE ARTIFICIAL SILK INDUSTRY

From immemorial prehistoric antiquity until almost the end of the nineteenth century, in the remains of clothing from old Egyptian mummies and from northern moorland deposits, as in modern clothing of the last decennia, we find as the essential basis of all textiles natural fibres in their original form, as provided to mankind by the animal and vegetable kingdoms, namely wool, silk, cotton, flax, hemp, nettle and jute fibres, and many others. The first idea of the production of artificial fibres of which we have evidence is dated 1734 and due to Réaumur, whose name has also been immortalized by the 80 degree thermometer scale. In his "*Mémoire pour servir à l'Histoire des insectes*" (Vol. I, page 154) he states that it should be possible to produce fibres of sufficient fineness from gum-lac or similar materials, as, after all, natural silk was nothing more than a solidified gum solution. This was, of course, merely a suggestion, the statement of a problem. The solution of the problem was still lacking.

A further 120 years passed by until a certain Audemars, of Lausanne, approached the problem and attempted its solution. In 1832 Braconnot obtained "Xyloidine," which burned very intensively, by treating all kinds of cellulosic materials with nitric acid, and thirteen years later, in 1846, Schoenbein, of Basle, obtained gun-cotton by treating cotton with a mixture containing nitric acid. Exact details of the manufacture of this compound were published in 1846 by Otto, of Brunswick, who thus acquainted wider circles with the process and with

the peculiarities of this new compound, which was considered to be a nitro-compound. This presumably pointed the way for Audemars. In 1855 he treated bast fibres, obtained from mulberry twigs, and carefully purified and bleached, with nitric acid. He dissolved the cellulose nitrate which he so obtained in a mixture of ether and alcohol, together with caoutchouc, and from the mass of collodium so obtained he drew threads with a steel needle, which solidified in the air. These threads were then wound on to a spool, which continued to draw out the thread from the mass in the act of reeling. This was already an achievement. (It may be mentioned that about 3,000 years ago, in China, threads were prepared in a very similar manner from the collected secretions of silk-worms.) The inventor obtained a British patent, No. 283 in the year 1855, but no practical application of the process ensued.

A process which was technically equally unimportant was described by E. J. Hughes in British patent 67 of 1857, and consisted in the production of silk-like threads by spinning a mass obtained from starch, glue, resins, tannins, fats, and so forth. We also mention the description by Ozanam (*C.R.* 1862, Vol. 55, page 833) according to which a solution of natural silk (in Schoenbein's solution) could be used, amongst other purposes, for the preparation of threads of indefinite length by imitating the action of the silk-worm by the use of spinning jets of various sizes. Here, for the first time, in contrast to the procedure of Audemars, we find a description of the principle universally used to-day for producing artificial silk. But all these suggestions once more lapsed into oblivion. Chemistry and technology were not yet ripe for the realization of the idea. More particularly, suitable and soundly designed apparatus was not yet available to replace the primitive methods of the time.

The next incentive to further experiments was provided by electrotechnology, which had developed continuously in the interval and required a suitable thread, which had to be as uniform as possible, for the production of electric lamp filaments, to replace the unsuitable bamboo filaments so far used.

Various methods have been proposed for the production of

such filaments. In 1889, J. W. Swan patented the use of cotton threads which had been gelatinized with strong sulphuric acid. A year later, Crookes proposed the production of filaments from a solution of cellulose in a cuprammonium solution. Robertson dissolved cotton in concentrated zinc chloride solution and drew threads from the viscous mass which he so obtained. Weston was probably the first to obtain threads from a solution of cellulose nitrate in a mixture of ether and alcohol (in 1883). The origin of the process of manufacture which later became general was probably the process of J. W. Swan described in British patent 5978/1883, and German patent 30291/1884, consisting in obtaining threads, by squirting or spinning, from a solution of cellulose nitrate in glacial acetic acid.

It is noteworthy that here we have the first practical instance, following Ozanam's suggestion (page 2), of the only process of filament production which is now practised, as the collodium solution was squirted through fine apertures into the coagulating liquid and the thread coagulated whilst being drawn, a method not dissimilar to that used by the silk-worm. More particularly, threads of indefinite length could be so obtained. By carbonization these threads were converted into filaments of pure carbon. In the first instance this was the only practical application of the invention, although the inventors, particularly Swan, endeavoured to make use of these wonderfully lustrous threads as a textile material. In the *Journal of the Society of Chemical Industry*, Vol. 4, 1885, page 34, there is a communication according to which samples of Swan's artificial silk were shown as a new textile material at the General Meeting of the Society of Chemical Industry in London on 4th December, 1884, and it is interesting to note that in this communication these threads are definitely described as "artificial silk." According to a communication to *Engineering* of 10th July, 1885, page 39, cloths made from Swan's artificial silk were exhibited at the Exhibition of Inventions held in London in that year, and, moreover, these cloths were made of denitrated material; for, in the interval, Swan had discovered a more or less practicable method of reducing the high inflammability of

his cellulose nitrate threads by treatment with ammonium sulphide.

Another method had then already been tried to reduce the inflammable properties of cellulose nitrate, namely, the use of a raw material other than collodium. In 1882 Weston had carried out experiments with the well-known solution of cellulose in Schweitzer's reagent (a solution of copper oxide in aqueous ammonia), and had obtained a patent for the process. Two years later Wynne and Powell prepared artificial threads from a solution of cellulose in zinc chloride solution.

During this period Count L. M. Hilaire Bernigaud de Chardonnet in France carried out experiments with collodium similar to those of Swan. He is alleged to have been inspired to carry out these experiments by the sight of the wood-pulp, with its silky lustre, discharged from the digester during a visit to the wood-pulp works of J. B. Weibel & Co., at Novillars (France). In 1884 Chardonnet handed to the Académie des Sciences in Paris a sealed memorandum containing exact descriptions of his first process of producing artificial silk, and his first patents (French patent 165,349, and German patent 38,368) were published in the following year (1885). The principle of his process hardly differed from that of Swan.

But, although artificial silk had thus been discovered and the technical and mechanical difficulties of the process been overcome in their main features, the working of such a process on a large manufacturing scale still met with considerable obstacles. In England the process was confined to the manufacture of carbon filament lamps, in the production of which the cellulose threads formed an intermediate product only. The intention of the English manufacturer, Lord Masham, to utilize Swan's process for the manufacture of artificial textiles on a manufacturing scale, was never realized. Various causes may have led to this result, more particularly the process was still too dear, compared with the price of natural silk, the only object at that time being the replacement of this latter material.

In France, on the other hand, Count Chardonnet persisted. His great and permanent achievement is that he solved the

industrial artificial silk problem, and by stern determination and heavy sacrifices, advanced it from its almost completed experimental stage to that of technical realization. He is, therefore, the true founder of the artificial silk industry. He was, however, not the only Frenchman to attack the problem of artificial silk. In Paris, M. P. E. Gérard sought in vain to achieve success with a mixture of gelatine and cellulose nitrate in acetic acid solution (German patent 40,373, Kl. 22, 1886). J. H. du Vivier also sought success by various combinations which are described in several patents (see German patent 52,977, Kl. 29, of 1889, and the later French patents of addition 195,655 and 195,656). The basis of his process was a mixture of three solutions, namely, gun-cotton in glacial acetic acid, fish glue in glacial acetic acid and gutta-percha in carbon disulphide. The thread, which had to be passed through a series of baths, was, however, without lustre. In order to obtain lustrous filaments the inventor recommends that one should mainly use gun-cotton in glacial acetic acid solution, together with a little castor oil. In spite of the complexity of the process it was utilized for a time by the Société Générale du Dynamite, of Rouen. But this silk, which was marketed as "Soie de France," disappeared entirely from the market after a short time.

The difficulties with which collodium silk had to contend consisted partly in its high price, which considerably exceeded that of real silk, but also in the absence of a good denitration process and the consequent great inflammability of the product. Not much value was attached to the denitration process, which entailed a considerable loss in weight, amounting to about one-third; moreover, it was found that denitration caused the fibre to be much weaker, when wet, than the original collodium fibre. Attempts were, therefore, made (for example, by du Vivier) to reduce the inflammability by impregnation with inorganic substances.

Count Chardonnet had also to cope with these difficulties. The Société Anonyme pour la Fabrication de la Soie de Chardonnet, at Besançon, which was founded in 1884 with a capital of 6 million francs, at first earned no profits, and

in 1890, when the capital had been reduced to $1\frac{1}{2}$ million francs, it was reconstructed with a further 6 million francs. Simultaneously, the works erected by Chardonnet at Spreitenbach in Switzerland fared no better, and soon had to close, although only temporarily. But the difficulties were ultimately overcome. Like all true inventors, Count Chardonnet's judgment was sound and far-seeing. He avoided complicated mixtures in the preparation of his solution. The only main ingredient of his threads was cellulose nitrate, or, rather, the cellulose hydrate into which this was transformed. The additions which he used were merely small amounts of reagents in order favourably to influence the character of the thread or to mislead his competitors. It was also evident to him that no success was to be expected without the help of a sound denitration process. He was well acquainted with the good and bad properties of cellulose nitrate by his work on explosives. His first artificial silk spinning machine was built for him by M. E. Mertz, of Basle, according to his instructions. He, and du Vivier also first showed to a larger public the new lustrous fibre at the Paris Exhibition of 1889. This still consisted of collodium threads which had not been denitrated, and were, therefore, readily inflammable. At Besançon, attempts to improve and cheapen the manufacture were pursued indefatigably on a large scale. Improvements in the spinning machinery and the composition of the solution, and also in the spinning process (concentrated solutions were spun directly into the air), but more especially the discovery of a good denitration process, finally led to success. In 1894 the shares of the company had fallen in value from 500 to 132 francs, but in the following year the first dividends were distributed. The Spreitenbach works also resumed manufacture successfully under new management.

In Germany, meanwhile, this field had not been neglected. The most successful worker at this time was Friedrich Lehner at Augsburg (later at Zürich), who had acquired knowledge of the Chardonnet process at Spreitenbach. By the use of a less viscous collodium solution, prepared with the addition of a trace of acid, he was able to dispense with excessive pressures and considerably to simplify the apparatus. He also twisted

several threads together immediately after spinning, which proved to be of advantage, as the twisted thread possessed considerably greater tensile strength. For spinning, a collodium solution was used, to which a solution of real silk (German patent 58,508 of 1890) or of vulcanized drying oil (German patent 82,555 of 1894) was added. Denitration was effected with ammonium hydrosulphide solution, to which a neutral magnesium salt was previously added, in equivalent proportion, in order to neutralize the harmful alkalinity. Lehner succeeded in interesting British capital in his process. A works was erected at Glattbrugg, Switzerland, in 1894. In this case, also, years passed before the various difficulties could be overcome, and before the critical period could be considered to be weathered, which occurred in 1898, according to the statements of Lehner himself. In 1900 the Vereinigten Kunstseide-Fabriken A.-G., Frankfurt-am-Main, was formed, which united under one company both the Chardonnet works at Spreitenbach and Lehner's works at Glattbrugg. Works were then built in Germany, one at Bobingen, near Augsburg, Bavaria, and the other at Kelsterbach-am-Main. An agreement was concluded with the Chardonnet Company at Besançon, which had itself erected further works, for example, at Sárvár in Hungary, at Padua and Pavia in Italy, and at Wolston in England, according to which the sole selling rights in Germany and Switzerland were accorded to the Vereinigten Kunstseide-Fabriken. Apart from the Chardonnet and Lehner patents this latter company had also acquired the interesting process of E. Bronnert, of Mülhausen, Alsace, according to which the nitrocellulose was dissolved in an alcoholic solution of calcium chloride, so that the use of ether was avoided. (German patent 93,009, Kl. 22 of 19th November, 1895.) However, experiments carried out according to this process at Glattbrugg gave rise to such difficulties in the spinning process that its technical exploitation was soon abandoned. An artificial silk works was also founded in Belgium at about the end of the century under the name of Société de Soie Artificielle de Tubize, which formed a temporary alliance of interests with the Vereinigten Kunstseide-Fabriken in 1906, and soon was followed by the formation of other firms

in that country, which did not, however, achieve the importance of the Tubize firm.

The increasing development of the young industry was much favoured by the fashions. After the initial distrust of consumers had been largely overcome and the value of the product had definitely been established, so that it had become a marketable commodity, the fields of its application increased. The Aargau hat-making trade, which had formed the first market, mainly for the manufacture of ribbons and so forth, was followed by further consumers, more especially the numerous works of the Barmen-Elberfeld trimming trade, which manufactured every possible kind of trimmings, tassels, embroidery, insertions, laces, fringes, ribbons, and so forth from artificial silk.

The economic effect of the rise of artificial silk was somewhat different to what had been anticipated. As indicated by the designation " artificial silk," which is not really justified from the chemical standpoint, it was originally intended primarily as a substitute for real silk, and it is not surprising that the producers of real silk endeavoured to defend themselves. In Italy attempts were made to induce the Government to take official action against the " artificial silk swindle." It was soon found that " artificial silk " was still by no means in a position to displace natural silk. The special qualities of the new product, which differed entirely from those of real silk, led to a demand which, for the time being, was largely in entirely different fields.

Meanwhile, the demand for artificial silk in the textile markets had grown to such an extent that the existing works were scarcely able to cope with it, and the prospects would have been exceedingly favourable, had it not been for the appearance of a competitive process, which appeared to offer considerable advantages over the Chardonnet process, namely, the cuprammonium process. The explosive properties of cellulose nitrate and, to a lesser extent, the danger of fire, and the high price of the mixture of alcohol and ether used as a solvent, all induced a search for some other solution from which artificial silk could be manufactured. Whilst preparing cuprammonium thiosulphate Schweitzer had discovered, in 1857, that the

cuprammonium solution obtained as a by-product had the property of dissolving cotton, and also linen, silk, and wool. (*Journal fur praktische Chemie*, 1857, page 109.) As already mentioned on page 3, Weston, an Englishman, in 1882, had already attempted to replace nitrocellulose solution by a solution of cellulose in copper oxide-ammonia (Schweitzer's reagent). He had patented the process, but it was never applied on a manufacturing scale. The Frenchman, Louis Henri Despaissis, met with no better fortune. In 1890 he obtained a patent (French patent 203,741 of 9th May, 1890) which claimed a process for the production of artificial silk from a cuprammonium solution. According to the statements of this patent a silky appearance could be imparted to threads of any cellulosic material by surface treatment with a cuprammonium solution, whereby, after precipitation, washing, and drying of the fibres, these were more or less provided with an artificial silk coating. It was difficult to obtain by this process a perfectly homogeneous, sufficiently concentrated and durable cuprammonium cellulose solution. The credit of having overcome these difficulties and developed the cuprammonium silk process on a successful manufacturing scale is due to the factory owner, Dr. Max Fremery, and the engineer, Johann Urban. They had been manufacturing carbon filaments for electric lamps, in the Rheinische Glühlampenfabrik Dr. Max Fremery & Co., Kommanditgesellschaft, Oberbruch (Aix-la-Chapelle district); these were produced from cellulose threads which were themselves manufactured (since 1892) from a cuprammonium cellulose solution. The sensation caused by Chardonnet's artificial silk products at the International Exhibition in Paris in 1889 and the consequent development of the nitrocellulose silk industry, supplied impulses which also directed the attention of the Oberbruch establishment to artificial silk manufacture. The two inventors soon succeeded in producing homogeneous and relatively stable cuprammonium cellulose solutions of a sufficient cellulose content, from which lustrous and sufficiently fine cellulose threads could be obtained, which were quite able to compete with the Chardonnet product on the world's markets. The observation was of importance

that the solubility of cellulose in cuprammonium solutions decreases with rise of temperature, and that the preparation of such solutions must, therefore, be carried out at a low temperature. For tactical reasons, the process was patented in the name of Dr. Hermann Pauly of München-Gladbach (later Professor of chemistry at Würzburg) in German patent 98,642, Kl. 29 of 1st December, 1897. It forms the basis of the whole cuprammonium silk industry and the starting point of other work in this field. The general principle of the process had certainly been published in the above-mentioned French patent, 203,741 by Despaissis, but Despaissis had evidently not produced any detailed and developed method of carrying out his principle ; such a process is described in the Pauly patent, which also includes several new factors, the inventive character of which it is impossible to deny. Urban constructed a suitable machine for spinning the solutions, which is described in Swiss patent 16,077 and is still widely used. Two years later, patents appeared in the names of Emil Bronnert, Max Fremery and Johann Urban, singly and jointly, describing various modifications and developments of the process. (German patents 109,996, 111,313, 119,098, 119,099, 119,230, 121,429, 121,430.) Although the process later underwent various changes, the above patents formed the basis for the formation of the largest and most important German artificial silk undertaking, the Vereinigten Glanzstoffabriken A.-G., founded on 19th September, 1899, at Aix-la-Chapelle, but which moved its office to Elberfeld in 1909. Manufacture was carried out in the first instance in two works, one at Oberbruch, near Aix-la-Chapelle, and the other at Niedermorschweiler, near Mülhausen, Alsace. A third works which was to have been erected at Glauchau, Saxony, was never built. During the succeeding years the process was developed by this firm to a high degree of perfection, by careful work and further improvements (see, for example, German patents 190,217/1904, 169,567/1905, 235,134/1906, 208,472/1907, 218,490/1907, and 229,863/1907), and soon proved to be equal if not superior to the Chardonnet process. This success induced the Vereinigten Glanzstoffabriken to found affiliated companies in other

countries. In France they formed La Soie Artificielle, Paris, with works at Givet and Izieux, in Austria, in 1904, the " Erste österreichische Glanzstoff-fabrik, A.-G., Vienna " (jointly with the Niederösterreichische Escompte-Gesellschaft), with a works at St. Pölten, which was opened in 1906 with a daily output of 125 kg. In England, the British Glanzstoff Manufacturing Co., Liverpool, was formed, with works at Flint.

As was to be expected, Chardonnet's invention had stimulated activity in other places than Oberbruch. A whole series of firms and inventors worked at the artificial silk problem, and many of them at the cuprammonium process, which owes many important improvements and even various fundamental changes to the activities of such workers. Details will be found in the special section of this volume dealing with the individual processes. Among many others we mention here, as being the most important, R. W. Strehlenert, the inventor of multiple spinning nozzles, and of revolving nozzles ; Dr. E. Thiele, the inventor of the stretch-spinning process ; Rud. Linkmeyer ; Ph. Friedrich, of Halensee ; E. W. Friedrich, of Blaton, Belgium, and J. P. Bemberg, A.-G. of Barmen-Rittershausen.

During this period a new process of manufacture of artificial silk appeared, forming a very weighty development, namely, the viscose process. In 1891, the Englishmen, Charles Frederic Cross, Edward John Bevan, and Clayton Beadle made the interesting observation that alkali cellulose reacts with carbon disulphide to form a water-soluble alkali salt, sodium cellulose xanthate. (See British patents 8700/1892, 4713/1896 ; German patents 70,999/1893, 92,590/1896.) The compound proved to be a typical colloid, yielding a viscous solution which the inventors named " Viscose." Lustrous threads of cellulose could be obtained from this solution, just as from collodium or cuprammonium solutions. A fairly satisfactory precipitation bath for spinning these viscose threads was discovered by Charles Henry Stearn in the form of aqueous solutions of ammonium salts, for example, ammonium chloride solution. (British patent 1020/1898, German patent 108,511, Swiss patent 19,135, U.S. patent 622,087.)

It is of interest to note that, as in the case of collodium silk,

the lighting industry supplied the first impulse in the case of viscose silk. Knöfler's invention of the manufacture of gas mantles from collodium silk suggested to Stearn that he should try to replace collodium by viscose for the same purpose. Prince Guido Henckel v. Donnersmarck of Neudeck, Upper Silesia, acquired Cross's and Stearn's German patents and erected an artificial silk works at Sydowsaue, for a daily output of 500 to 600 kg. of silk under the name of "Fürst Guido Donnersmarcksche Kunstseiden und Acetatwerke." Although a better spinning bath for viscose silk was discovered in these works by M. Müller and P. Koppe, in the form of a bisulphate solution (German patent 187,947/1905), success only came very slowly. The chief difficulties were only overcome about the year 1910, following on various changes more particularly in the method of spinning, and after the spinning-bath of Müller and Koppe had been further improved by Hottenroth by the addition of a neutral salt to the disulphate, thus avoiding the presence of free sulphuric acid. In the following year (1911) the works were taken over by the Elberfelder Glanzstoffabriken, who soon developed the viscose process in Germany with great success.

In England, the firm of Samuel Courtauld & Co., Coventry, had acquired the patent rights of Cross and of Stearn in that country. In a comparatively short time they proved the utility and extraordinary importance of the viscose process by placing on the market an exceptionally beautiful silk. The consequence was that new viscose silk works were built, not only in Germany, but in other European countries and in America, for example, in Emmenbrügge (Switzerland), Turin, Dieppe, Alost (Belgium), Barcelona, Moscow, Chester (U.S.A.), and elsewhere. According to English sources there were already 30 viscose silk works in 1917.

The Chardonnet process was also further improved in various directions during these same years.

Thus, in spite of various failures,[1] a steady development of the artificial silk industry, as a whole, was a feature of the

[1] Thus, for example, works at Wolston (England) and at Fismes (France) were closed.

early years of the present century. The large number of patents dealing with artificial silk demonstrate the intensive activity of inventors during this period, and it is in no way surprising that the successes of a few works and the extraordinary dividends distributed by a few firms induced numerous new companies to be formed. During the next few years, therefore, a large number of new artificial silk works were erected both in Germany and in other countries.

But the further we pursue the historical development of the artificial silk industry, the more must we confine ourselves to general statements. A description at this point of all the numerous new companies would be devoid of the interest which attaches to the pioneering work of the earlier firms which has just been described, just as a description of a new South Polar expedition could never hope to attract the interest with which we read of Amundsen's and Scott's first victories over the South Pole. It will suffice to state here that there were already 22 artificial silk works in 1906. Of these, 7 were in Germany and 6 in France. Of the remainder, there were 4 in Switzerland, 3 in Italy, and 2 in England.

An important factor in the development of the industry was the circumstance that not only was ordinary artificial silk manufactured, each thread of which consisted of a bundle of many individual fibres, but that at an early stage, thicker individual fibres (monofil) were produced, which became known as " artificial horsehair," and found extensive use, for example, in the form of plaited material for women's hats, for tassels, trimmings, and so forth. There were even periods during which the demand for ordinary artificial silk was so small that the demand for artificial horsehair almost entirely maintained the works in activity. Ribbon-shaped single threads were also produced and were used for the same or similar purposes.

During this period of development attempts were not lacking to produce artificial silk from non-cellulosic materials. More particularly there were constantly recurring attempts to produce a fibre identical or similar to natural silk in chemical composition. Gelatine, casein, albumen, fibroin, natural silk waste and similar materials were all tried. We will return to

these attempts when describing the individual processes. None of them met with success of more than a very transitory character, such as was enjoyed by the process described by C. Millar in German patent 88,225 (1895); the product which was produced from gelatine was marketed by an English company under the name of "Vandura silk" but very rapidly disappeared.

Better success was achieved by a further new product, produced from cellulose acetate. The workers in this field comprised the Americans, Mork, Little, and Walker, also Leonhard Lederer, the Fürst Guido Donnersmarcksche Kunstseiden-und Acetatwerke, the Farbenfabriken vorm. Friedrich Bayer & Co., of Elberfeld, Chemische Fabrik Knoll & Co., of Ludigshafen, Henri Dreyfus, of Basle, and others. Although acetate silk has only just achieved economic success, after experiments extending over the last thirty years, no final opinion can even now (in 1925) be expressed on this product. It is by no means excluded that this silk may play an important part in the future, for its relatively great resistance to water, compared with silks consisting of cellulose hydrate, is certainly a considerable advantage. The difficulties which were encountered in producing a marketable product, more especially one which showed a satisfactory and uniform affinity for dyestuffs, were very great, and for a long period prevented the commercial exploitation of this material. Only very recently have these difficulties been mastered to such an extent that the process has proceeded beyond the experimental stage to the erection of fairly large works. British Celanese, Ltd., Spondon, and the allied enterprise, the American Cellulose and Chemical Co., Cumberland, U.S.A., operate according to the process of Henri Dreyfus, the Managing Director of the former company. There is another acetate silk company in America, the Lustron Company, Boston. The Cellulose Company of America, Chester, closed their small works in 1924.

We must finally refer to further cellulose compounds, the properties of which appear to render them suitable for the production of artificial silk, namely, the cellulose ethers, which were first prepared during the same period. The great stability

towards water of many of these compounds, their solubility in organic solvents and other properties, led to great expectations. (See also page 16.)

Thus, the 25 years of active and strenuous endeavour, starting with Swan and Chardonnet—from 1885 to 1910—led to the development of four important artificial silk manufacturing processes, together with a fifth process of which the future is yet uncertain. The succeeding years, almost to the present moment, have not altered the position essentially, and thus to-day the same four processes alone supply the whole of the artificial silk produced on a manufacturing scale, although the relative outputs of these processes have altered very considerably.

The Great War, which falls within this period, led to great technical and economic difficulties for the industry. A large number of artificial silk works lying within or near the war area, such as the German works on the Belgian and Dutch frontiers, and in Alsace (Niedermorschweiler), the numerous Belgian works (Tubize), the French works at Fresnoy and Givet, the Russian works at Sochaszew and Tomaszow, were directly affected. The other works suffered mainly through the conscription of their trained staff and workpeople, and also, more particularly in the territories of the Central European powers, through lack of necessary materials, such as coal, sulphur, copper, oil, soap, rubber, glycerine, and so forth. For these reasons many works outside the actual war area had to close ; others had to turn to the manufacture of other articles, whilst some were merely forced to reduce their output. The Vereinigten Kunstseidefabriken, Frankfurt-am-Main, converted their works at Kelsterbach, during the war period, into an establishment for desiccating meat and vegetables. The Bobingen works were sold to the Köln-Rottweiler Pulverfabriken and used for the manufacture of gun-cotton.

On the whole, however, the war did not retard the development of the artificial silk industry, for it resulted in a large number of compensating stimulating factors ; these ultimately predominated over the depressing influences, when once the main difficulties had been overcome, to such an extent that

the final result was a decidedly stimulating effect on the artificial silk industry, both during the war period itself and subsequently. New and higher qualities were demanded of artificial fibres. In Germany and Austria, for example, the whole output of artificial silk was for a time requisitioned for military use in cartridge holders, fuses, gas masks, and other munitions, in order to replace cotton, wool, and silk, which all became increasingly difficult to obtain as the war continued. This was particularly true in the case of the Central European States, in which it applied not only to the requirements of the army, but also to those of the civilian population. Staple fibre then made its appearance. This material consists of artificial silk, the thread of which is cut into sections of about the length of cotton or worsted staple, namely 3 to 6 cm., which are then treated on a carding machine and so forth, similarly to natural fibres, and finally spun to yarn. Even before the war artificial silk waste had already been treated in similar fashion, more particularly by worsted spinning mills, for example, for the production of mixed colour effects in woollen yarn and so forth. Such substitutes for animal and vegetable fibres, both for clothing and for technical purposes, were very much used during the war period, more particularly in Central Europe. In addition, the production of real silk declined by one quarter during the war. All these circumstances ultimately led to such an increase in the demand for artificial silk that steady extension of the works and increased production became grave necessities and that finally, even firms which had had to fight hard for their existence before the war were able to earn large profits. Existing works were enlarged, new works were erected, and new firms were founded.

After war had ceased, this development continued unchecked. A novelty of special interest during the post-war period was the production of cellulose ether silk, from the cellulose ethers already referred to, although on an experimental scale only. The work of Dr. Leon Lilienfeld was of fundamental importance in this field, which was also successfully developed by the Elberfelder Farbenfabriken. Up to the present, however, a final verdict on the manufacturing possibilities of this new

fibre can be given with even less certainty than on those of acetate silk. It appears doubtful whether it will be possible to produce the material sufficiently cheaply, and whether its properties, and more particularly its dyeing properties, will comply with requirements. The great stability against every kind of outside influence possessed by those cellulose ethers, insoluble in water, which are alone of interest for artificial silk manufacture, is a highly desirable quality. This stability is so exceptional, compared to that of all other varieties of artificial silk, that a successful development of the process would certainly be of fundamental importance for the industry.

For the rest, the work of the last few years has consisted in further development of the existing processes, improvements and simplification of the machinery, increased fineness of the fibre and increase of its tensile strength, and, last but not least, the production of a better cellulosic raw material, especially suited to the requirements of artificial silk manufacture. The particularly important advance, due to continued efforts, is the increased approximation of the properties of artificial silk to those of real silk. Even with regard to the external properties, the unpleasant, crude, glassy lustre of the fibre is now avoided if possible, and artificial silk is produced with the soft and quiet sheen of real silk. The strength of the fibre has been notably improved, its dyeing properties are in general excellent and, with regard to fineness, it is now possible to produce fibres even finer than those of natural silk. The improved properties naturally extend the field of application. The demand steadily increases, and the output has become incredibly large ; the figures given in the Economic and Statistical Section of this book tell their own tale. Artificial silk is now by no means confined to its original fields of application, it is steadily gaining on real silk in its own particular and peculiar field. For many years one has been justified in speaking of the serious competition of artificial silk with real silk. For example, since the war the enormous production of artificial silk in the United States has resulted in a considerable decrease in the importation of real Japanese silk into that country.

Thus, not only has the dream of the first inventors been

realized, but it has been greatly surpassed by the reality. Although setbacks may occasionally occur, due to changes in fashion, to over-production or other causes, these will be of a temporary character only, and even to later generations the history of artificial silk will appear, as I described it several years ago, as a " triumph of human experimental skill."

CHAPTER II

THE MANUFACTURE OF ARTIFICIAL SILK

Manufacture of Artificial Silk in General. If a natural, uncut, and, therefore, ordinary looking diamond is placed next to a splendid brilliant in a gold setting, in order to show what the human hand can effect on a rough stone, many a person will be filled with amazed admiration at the great difference between the two objects. But this difference is, indeed, small compared with that between a log of spruce, straight from the woodland, and a wonderful fabric of artificial silk. An observer of these two articles would be more astonished than the other if told that the fabric was produced from the log by human art and industry. Many would shake their heads in sheer incredulity and the others would realize the large amount of arduous endeavour that was represented by the transformation. The purpose of the following chapters is to describe these transforming processes.

We will first consider the production of artificial silk in general, that is, we will investigate the various methods and contrivances which are common to all the various methods of manufacture. This general description will be divided into three subsections, on the production of the spinning solution from the raw material, the spinning process by which the fibre is formed, and the finishing of the fibre, that is, its further treatment to form the finished product.

Each of these chapters will be further subdivided. In treating of the production of the spinning solution we will have to deal with the raw material and the actual spinning solution ; when describing the spinning process we must consider the actual spinning operation, the spinning baths, and the spinning mechanism ; and, finally, the finishing processes include washing, bleaching, drying, reeling, and so forth. Dyeing, finishing, and so forth should actually also be included under that heading,

but for reasons which will be given later they are dealt with in special chapters.

THE PRODUCTION OF THE SPINNING SOLUTION

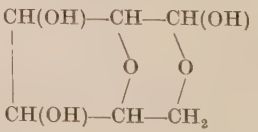
The Raw Material. All artificial silks at present manufactured, or the manufacture of which appears possible in the present state of technology are composed of cellulose derivatives, some of them of cellulose hydrates, which are closely related chemically to cellulose itself, whilst others are composed of cellulose esters, that is, derivatives of cellulose with acids, or, finally, of cellulose ethers, that is mixed anhydrides of cellulose and alcohols. We will revert to these various classes of derivatives later. Apart from certain other raw materials, the use of which has been tried experimentally, and to which we will also briefly refer again later, the basic raw material for the present manufacture of artificial silk is exclusively cellulose, the essential structural component of almost all plants, which is also, in consequence, the most plentiful carbohydrate.

Properties of Cellulose. Chemically, cellulose is, as already mentioned, a carbohydrate, being a polysaccharide of the formula $(C_6H_{10}O_5)_x$. It contains free hydroxyl groups, and is, like the sugars, an alcohol. It is, therefore able, like all alcohols, to form alcoholates, ethers, and esters, and, in fact, behaves in general as a trivalent alcohol, that is, it contains three free, reactive hydroxyl groups, on the basis of the C_6 formula. Iodine colours cellulose yellow to brown. A solution of iodine and zinc chloride or of iodine in sulphuric acid produces a characteristic blue coloration. The presence of water appears to be essential for this latter reaction. Cellulose is relatively stable towards alkalis. Concentrated solutions of alkali hydroxides form alkali-celluloses, such as $(C_6H_{10}O_5)_2$ NaOH, which are presumably alcoholates. Alkali-cellulose is an important intermediate product in the production of viscose silk (see page 258 *et seq.*), of cellulose ethers (see page 322 *et seq.*), and other cellulose derivatives. The alkali is completely liberated even by water, with recovery of cellulose. The recovered cellulose, however, shows somewhat altered properties, such as increased affinity for dyestuffs, is more hygroscopic

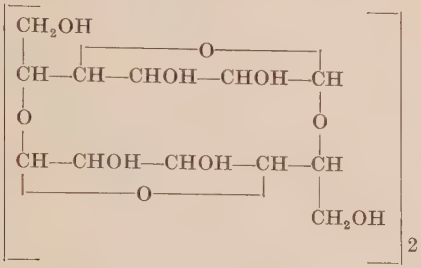
and more easily hydrolysed, and is usually considered to be a cellulose hydrate, although, in fact, it may have merely undergone some change in its colloidal condition, with adsorption of water. A typical cellulose hydrate of this type is represented by mercerized cotton, such as is produced when cotton, in the form of hanks, is treated in the cold with concentrated alkali hydroxide solution whilst under tension. Cellulose is less stable towards acids. Even dilute acids, by action for a long period or at high temperature, convert cellulose into hydrocellulose, which forms a brittle material, readily reduced to a powder by rubbing, and consisting of a mixture of unaltered cellulose and products of decomposition. Oxidizing agents also produce similar friable materials, the oxycelluloses, the formation of which causes the rotting of cotton and linen fabrics when overbleached. Concentrated sulphuric acid first converts cellulose into amyloid or dextrinoid substances known as Guignet cellulose, cellulose parchment, and so forth. The most important cellulose derivatives from the technical standpoint are the cellulose esters, which are produced by the action on cellulose of moderately concentrated acids or acid anhydrides, if necessary in the presence of a catalyst. The most important cellulose esters are the readily inflammable cellulose nitrates, sometimes wrongly designated as nitrocelluloses. These are prepared both as lower nitrates, soluble in a mixture of alcohol and ether, and known as collodium cotton or celloxylin, and as higher nitrates, insoluble in a mixture of alcohol and ether, and known as gun-cotton or pyroxylin. Collodium cotton forms the basic material of the oldest artificial silk process (see Collodium silk) and is also used for manufacture of collodium, celluloid, celluloid varnishes, and so forth. With acetic anhydride and a dehydrating agent, such as sulphuric acid or zinc chloride, cellulose forms cellulose acetic esters, acetylcelluloses or cellulose acetates, which are used for similar purposes to the nitrates, such as the manufacture of artificial silk, celluloid substitutes, and varnishes, but possess the advantage of not being dangerously inflammable. (See Acetate silk.) Esters of other acids are at present of no importance to the artificial silk industry. An interesting and technically important

reaction is that between alkali-cellulose and carbon disulphide, with formation of alkali-cellulose xanthate, the aqueous solution of which forms the so-called " viscose," which is the main intermediate product of that artificial silk process which is at present the most important. (See Viscose silk). Finally, we must mention the cellulose ethers, which are produced similarly to ordinary ethers, for example by the interaction of alkali-cellulose with alkyl sulphates or chlorides. The more highly alkylated of these ethers, which are insoluble in water, have also been used for manufacture of artificial silk. (See Cellulose ether silk.) By complete hydrolytic dissociation, for example by first hydrolysing with sulphuric acid of about 73 per cent concentration, to form cellulose-dextrines, and then boiling these for some time with dilute acid, cellulose is quantitatively converted into grape sugar, $C_6H_{12}O_6$, which compound is, therefore, the structural unit of the cellulose molecule. It must be assumed that an intermediate stage in this hydrolysis is the formation of cellobiose, a compound which it has not been found possible to isolate during " sulpholysis " with sulphuric acid, although in 1899 Skraup isolated the acetate of cellobiose during " acetolysis " with a mixture of acetic anhydride and sulphuric acid, whereby he simultaneously effected acetylation. From the acetate so obtained Skraup isolated cellobiose itself. This compound is obtained from its alcoholic or aqueous solution in the form of a crystalline mass, which melts with decomposition at about 225° C. During acetolysis the production of cellobiose is accompanied by that of its isomer, celloisobiose, discovered by Ost and Prosiegel in 1920, and which crystallizes in fine needles, melting at 190 to 195° C.

The constitution of the cellulose molecule is still quite unknown, and the various suggested formulae are all in dispute (see also K. Hess). The following formula of Green, or possibly a polymer of the same, is in almost complete conformity with the behaviour of cellulose—



In the light of later investigations, more particularly on the dissociation products of cellulose, the following formula of R. O. Herzog and P. Karrer is preferred by many—



The property of cellulose and of most of its compounds which is most important for the production of artificial silk, is that of forming colloidal solutions in certain media. Thus, cellulose itself is soluble in aqueous solutions of copper oxide and ammonia (Schweitzer's reagent), and can be recovered from this solution in solid form. (See Cuprammonium silk.) This is also true of the above-mentioned solutions of cellulose xanthate, of the various cellulose esters (the nitrates and acetates), and of the cellulose ethers.

With regard to the raw materials which may serve as sources of cellulose, Chardonnet already published a whole number in 1890 in his German patent specification 56,631, Kl. 29. He says: "One uses purified cellulose, which may have been prepared from wood-pulp, straw-paper, cotton, rags, filter paper, hemp, ramie, or the like." But he certainly merely mentioned the majority of these materials in order to secure his position, for, in practice, he only considered cotton. As the artificial silk process necessitates the greatest possible uniformity of the raw material, and the daily output of the various works has increased very greatly, it is only possible to use such raw materials as can be obtained in unlimited quantities and of almost uniform quality. Such materials are more particularly cotton and wood-pulp.

CHAPTER III

COTTON

Cotton, which was known in the East, in addition to flax and wool, more than two thousand years before our era, and which has been one of the most important raw materials of the world's trade for a considerable time, consists of the fine fibre cells which enclose the individual seeds of the cotton plant (genus *Gossypium* L.), and which protrude from the bursting seed capsule as a felty tuft on ripening. The genus Gossypium belongs to the family of the Malvaceae. The original home of cotton is probably to be sought for in India, from whence it spread round the earth and is cultivated in the tropical and subtropical zones, mainly of the Northern Hemisphere. In consequence of varying methods of cultivation, climatic influences and so forth, a number of varieties of cotton have been evolved in the course of time, and of these certain species only are cultivated or favoured in any one country.

The most important of these species are—

1. *Gossypium herbaceum* (L.), the white herbaceous cotton plant, from which most East Indian cotton plants are derived, forms a summer growth, ⅔ to 1 metre in height. Its probable origin was in Arabia or Persia, or perhaps even in India. It is cultivated, in numerous varieties, in China, Japan, India, Annam, Siam, Ceylon, Java, the Levant, Asia Minor, Africa (Egypt), and Malta. The fibre from the seed capsule is rather short (staple 13 to 23 mm.), and is usually white and lustrous, but occasionally yellowish and dull.

2. *Gossypium arboreum* (L.), the arboraceous cotton plant, with a woody stem, usually 2–2½ metres, but sometimes more than 5 metres high. The fibre resembles that of the above-mentioned species, but is usually slightly longer. Its colour is usually yellowish. It is cultivated in China, India, Asia Minor, Africa, Italy and Spain. There are varieties named *G. rubrum*, *G. roseum*, *G. purpurescens*, and others.

3. *Gossypium barbadense* (L.), the West Indian cotton plant, which has, like the last-named species, a tall, woody stem. It is the most commercially important species of cotton. Most varieties of American cotton are derived either from this species or from *G. hirsutum*, which will be described later. It supplies the so-called Sea Island cotton, which is in special demand on account of its long staple (up to 50 mm.).

The Egyptian Macco cotton and the so-called Caravonica cotton are

varieties of, or crosses with, this species, which is mainly cultivated in Central America, in the Antilles, Georgia, South Carolina, Florida, Brazil (including Pernambuco), and also in Egypt.

4. *Gossypium hirsutum* (L.), is, in spite of its short staple (15 to 40 mm.), the most important species excepting *G. barbadense*, and supplies the greater part of the cotton produced in the United States (Upland, Louisiana, Texas, etc.). The so-called Long Staple Upland cotton, which is of great commercial importance, is derived from a cross between the Sea Island and Upland species. It is mainly cultivated in Central and North America, but also in China, India, Siam, Persia, Australia, East Africa, and Southern Europe.

5. *Gossypium peruvianum* originally came from Peru, is mainly grown in Brazil and Peru, and is very similar in character to *G. barbadense* (No. 3), but has a shorter staple, which averages about 30 to 36 mm.

The species known as *G. vitifolium* (L.), *G. glabrium* Lam., *G. punctatum* Schum., *G. maritinum* Pod., and *G. glabratum* Pod., are varieties of *G. peruvianum*, and *G. barbadense*.

6. *Gossypium religiosum* (L.), the Chinese or yellow cotton plant, a shrub 1–1½ metres high, is considered by some to be merely a variety of *G. peruvianum*, whilst others consider it to be a cross between *G. barbadense* (L.) and *G. hirsutum* (L.). It is mainly cultivated in India and China. Its yellow and reddish brown fibres form the Chinese " Nankin " cotton.

The cotton fibre is a uni-cellular seed-hair which, in contrast to the wood-pulp fibre, has a natural point at one end only, as the other end is torn away from the seed to which it was attached. Under the microscope the fibre appears as a broad band, free from knots, with a more or less wide lumen, often spirally twisted owing to the stresses induced by drying (Fig. 2), and like a collapsed tube in cross-section.

No differentiation of the tissues is observable by direct microscopic observation of the cotton fibre. If, however, it is submitted to the action of gelatinizing agents or solvents, such, for example, as a solution of copper oxide in ammonia, differentiation into layers is plainly apparent, as was shown by A. Herzog, especially in the presence of selective dyestuffs. Excellent results are obtained with ruthenium red and somewhat less good results with safranine ; chloramin may also be used. The following portions can then be distinguished. The seed-hair is covered externally by a dense layer, the so-called cuticle, which is about 0·5μ thick, and has a more or less wrinkled or granular surface. Inwardly this adjoins a strongly swollen

layer of almost pure cellulose, the true cell wall, the inner surface of which, adjoining the central cavity, is bounded by a thin inner skin, more or less strongly infiltrated with albumens. The central channel itself, the lumen, is partially filled with protoplasmic residues, pigment, etc. The cuticle must be considered as the chemically modified outermost layer of the cotton fibre. According to Haller (*Zeitschrift für Farbenindustrie*, 1907, page 126), its existence is essentially due to the cutin present in the outermost layers. As was shown by Herzog, the cuticle plays an essential part in the natural coloration of the cotton, as the natural pigments are mainly located in the included bodies and in the cuticle. In the case of the strongly coloured Nankin cotton only, the cell wall and the inner coating are also coloured yellowish-brown. According to A. Herzog the resistance to wetting of the untreated fibre is not to be ascribed to the cuticle, but essentially to the included fatty bodies. According to the same investigator the cuticle has also no practical influence on the absolute strength of the fibre, which is entirely governed by the absolute cross-sectional area of the cell wall, which amounts to 157 to 339$\mu\mu$.

Fig. 2. Cotton
Magnification 100

The cuticle behaves optically as an isotropic and, therefore, singly refracting body. Under the microscope, it appears to be optically empty. The conversion of the outer layer into cuticle is obviously, therefore, accompanied by physical as well as chemical changes.

R. O. Herzog publishes details on the histological structure of the cellulose fibre in Papierfabr., 1925 (*Vereinsbeilage*, page 121). According to him the cells, or individual fibres, the average width of which

is 20–30μ (seldom over 100μ or under 5μ), do not represent the ultimate structural element of the cotton fibre. On the contrary, they are built up of very small units, the primary fibres or fibrils, which can easily be observed microscopically, especially after mechanical treatment (for example, in the colloid mill) followed by gelatinization. Microscopic observation by ultraviolet light of a series of such fibrils indicated a width of a few tenths μ, so that about 100 such fibrils would have to be laid side by side in order to attain the width of a single fibre. It was, however, found that with the help of Röntgen rays the fibrils could be resolved into still smaller structural elements, the width of which amounted to a few $\mu\mu$ (millionths of a millimetre) only, so that about 100 of these smallest elements would again have to be laid side by side in order to attain the width of a fibril. These smallest elements were characterized by their optical behaviour as crystals and are called crystallites.

These ultimate elements are embedded in, or cemented together by, certain accessory substances, and it is assumed that many changes in properties which were formerly ascribed to changes in the cellulose molecule (for example, the reducing powers of hydrocellulose and oxycellulose) are really due to changes in these accessory substances. More particularly it is supposed that no depolymerization of the cellulose molecule occurs on hydrolysis. It remains to be seen whether these hypotheses will receive further confirmation.

The fact is, at any rate, firmly established that the cellulose molecule, as supplied to us by Nature, consists of a molecular complex corresponding to a multiple of the formula $C_6H_{10}O_5$. This complex never goes into solution as such, but solution is always preceded or accompanied by more or less intensive depolymerization or de-aggregation. We will return to this subject later, as the manufacture of artificial silk in particular affords many examples of these phenomena. (See, for example, page 65.)

The density of cotton fibre is 1·47 to 1·50. The mean length of fibre (staple) varies from 12 to 58 mm. Long staple qualities have a mean fibre length of 25 to 40 mm., and short staple qualities of 10 to 25 mm. The width of cotton fibres is from 0·012 to 0·045 mm.

Chemically, cotton consists of almost pure cellulose $(C_6H_{10}O_5)_x$ with all its typical properties. (See above.) Apart from cellulose and about 7 to 8 per cent of moisture, cotton contains fatty substances, albumen, proteins, mineral substances, and pigments. According to Georgievics its quantitative composition when air-dry is: 87 to 91 per cent cellulose ; 7 to 8 per cent

water; 0·4 to 0·5 per cent wax and fat; 0·5 to 0·7 per cent protoplasmic residues; 0·12 per cent ash, and traces of dyestuffs. In crude, unbleached cotton the percentage of cellulose is, of course, lower, owing to the presence of impurities. According to an analysis of the Testing Station of the State of Tennessee, the crude fibre of an American cotton contained: 83·71 per cent cellulose; 6·74 per cent water; 0·61 per cent wax and fat; 1·50 per cent proteins and albumens; 5·29 per cent non-nitrogenous extract; 1·65 per cent ash. In very impure cotton samples, particularly from India, the ash contents frequently amount to 5 to 6 per cent. According to C. Schunk, the fatty constituents are of two kinds, namely cotton-seed oil and cotton wax, which latter is very similar to carnauba wax and is soluble in Turkey red oil.

One may assume that during the bleaching process crude cotton loses on the average about 5 per cent by weight. The ash contents, which amount to 0·9 to 1·8 per cent, may be reduced by the bleaching process to 0·03 to 0·05 per cent. Usually, however, they amount to about 0·1 to 0·4 per cent in the bleached material. The following occur in the ash: potassium carbonate, potassium chloride, potassium sulphate, sodium carbonate, magnesium phosphate, iron oxide, alumina, magnesium carbonate, calcium carbonate and silica. The ash of bleached cotton consists mainly of silicates.

Water dissolves the greater portion of the ash constituents. If cotton is boiled with water, about 2 per cent of the fibre weight is removed in the form of soluble materials. On evaporation of the water, an extracted residue is left consisting of a gummy, very hygroscopic, brownish yellow mass, which contains about 40 per cent of ash, mainly potassium carbonate.

The proportion of nitrogen in cotton, due to the albumen contents, amounts on the average to 0·3 to 0·5 per cent. A. Herzog was unable to confirm the statement by Bowman in his book, *The Structure of the Cotton Fibre*, that nitrates are present in cotton. According to Herzog, ruthenium red and ammoniacal copper oxide form an excellent reagent with which to detect the albumens and the cuticle under the microscope. Albumen is usually quite irregularly distributed within

the fibre. The albumens frequently cover the walls of the inner layer, within the lumen, and remain behind as a folded, tubular structure, when the cellulose is dissolved. Occasionally, the seed-hair is quite free from albumen. The proportion of albumen varies greatly in the various varieties of cotton, as is shown by the following table of nitrogen contents, which were determined by A. Herzog—

Cotton	Nitrogen per cent	Cotton	Nitrogen per cent
Indian (Comillah)	0·20	Upland . .	0·30
Togo . . .	0·31	West Madras .	0·45
Caravonica . .	0·31	Indian (Tinnevello)	0·45
Chinese . .	0·34	Egyptian (Africa) .	0·51
		,, (Joanovic)	0·56

Under the polarizing microscope the albumen appears singly refractive.

On bleaching, the cuticle of the cotton fibre is almost completely destroyed, as are also the albumens and the natural pigments which are generally associated with the latter. The nitrogen contents of bleached cotton are, therefore, very low, namely, 0·002 to 0·003 per cent.

As alkalis attack the cuticle but little or not at all, the more brilliant lustre of cotton which has been treated with alkali is not due to the absence of the cuticle, as was formerly supposed, but is obviously connected with phenomena of gelatinization at the surface. Cotton behaves with alkali in accordance with what was stated about the action of alkali on cellulose in general, on page 20 above. This behaviour is of importance in the artificial silk industry, as alkali-cellulose is an intermediate product in the production of viscose silk.

The behaviour of cotton with a solution of copper oxide in ammonia is of equal interest, as this reaction is the basis of one of the most important methods of manufacturing artificial silk. We will discuss this reaction more fully in the chapter on Cuprammonium silk.

Fibres which have been incompletely developed through lack of ripeness or for other reasons, the so-called " dead " fibres,

occasionally occur among the normal fibres, in varying amount according to the variety of cotton. They are said to be frequently found in Indian varieties of cotton, but are scarcely ever found, for example, in *Gossypium barbadense* (L.). The twist which is so characteristic of the normal cotton fibre under the microscope is entirely absent in the dead fibres. Frequently, also, there is no lumen. The tensile strength of these dead fibres is very slight ; they have either bad or abnormal dyeing properties and dissolve very slowly in ammoniacal copper oxide solution, without displaying the characteristic barrel-shaped swellings which characterize this reaction with ripe fibres. (See Fig. 82, page 229). With iodine in potassium iodine solution they give a light yellow coloration only. Vat dyestuffs dye the dead fibres either faintly or not at all, but, on the contrary, they are more intensively dyed by substantive dyestuffs than the normal cotton fibres. In the unripe fibres the cuticle is either missing entirely or is very weakly developed ; consequently, they are immediately dissolved by concentrated sulphuric acid. Whereas the ripe fibres appear brightly illuminated in polarized light between crossed Nichols, in consequence of their doubly refracting properties, the dead fibres show no double refraction. Obviously, these properties are due to marked differences between the ripe and unripe cotton fibres with regard to both physical structure and chemical composition. (See Wiesner, *Rohstoffe des Pflanzenreichs*, Vol. 2, page 248 ; R. Haller, *Beitrage zur Kenntniss der toten Baumwolle Chem. Ztg.*, 1908, page 838.)

Regarding the use of cotton in the artificial silk industry, good, long staple spinning cotton, with a staple of as much as 40 mm. and more, was at one time used as a raw material, but is now much too dear. The various forms of cotton waste can alone be used for artificial silk manufacture. These are, more particularly, the so-called linters, which remain attached to the seed when the cotton is ginned, and are comparatively long, and the neps or virgin fibres, short hairs which form a fine down on the seed capsules of various varieties of cotton, alongside the long seed-hairs. The linters are recovered, together with a part of the virgin fibres, before the seed is

pressed for the recovery of cotton seed oil, and the remainder of the virgin fibres are recovered by a special process, the Minck-Segundo process, from the crushed capsules after pressing. These are frequently used in admixture with the linters.

In order to recover the linters, the seed from which the main portion of the cotton has been removed in the ordinary gin is passed through another machine of somewhat different construction, the so-called linter-gin. This is a saw gin, in which the teeth are closer than in an ordinary gin, but which otherwise operates in precisely the same manner. Such a machine is capable of treating 5,000 to 6,000 kg. of cotton seed in 10 hours and recovering 350 to 400 lb. of linters from that quantity of raw material.

There are also available large quantities of spinning waste (combings, etc.) which are recovered during the spinning of cotton.

All these raw materials are naturally greatly contaminated by admixtures of all kinds and have to undergo a careful preliminary treatment before they are fit to be used for the preparation of spinning solutions. Further details regarding this preliminary treatment will be given in the next chapter but one.

CHAPTER IV

WOOD-PULP (WOOD CELLULOSE)

By the term wood-pulp we denote the fibre obtained from the walls of isolated wood cells.

Structure of the Cells. We may remind the reader that the unit element of plants, the cell, comprises an outer cell wall, and that in the case of all living cells this encloses the protoplasm, which is a member of the albumenoid group, the starch-containing nucleus and the saline cell sap. The thin, colourless, transparent, elastic cell wall consists essentially of pure cellulose, impregnated with mineral matter and saturated with water. In the course of the conjunction of individual cells to form cellular tissue, the steady growth of the plant and the differentiation of the function of the individual cells in the higher plants, the cells develop into forms of very varying character. In wood, three main forms of cells can be distinguished, according to form and arrangement, prosenchyma, parenchyma and sclerenchyma cells.

1. Prosenchyma cells are usually narrow, long, spindle-shaped or thread-like, more or less thick-walled cells, usually with pointed or narrowed ends. (See Fig. 3.) They include, for example, bast fibre cells, the tracheides of wood, the cotton fibre, and many others. We are here mainly interested in the tracheides and vessels of wood, which are both included in the wider term, tracheae. In wood, both these types are " empty " cells, from which the protoplasm originally present has disappeared, after which they have assumed the functions, more particularly of conducting water through the plant organism, but also partially of storing nutrient materials. With the growth of the plant and extension of the individual cells more or less thickening of the cell walls occurs, and is often very considerable. This may either take place over the whole surface of the cell wall, or at certain portions only, in the form of rings, spirals, ladder-like markings, reticulations and so forth. Frequently,

the cell walls are of uniform thickness, but are perforated by transverse canals, which communicate with canals from adjacent cells and so facilitate the circulation of the sap. From the side of the fibre these canals are, naturally, seen as round openings, that is, as small circles, commonly known as pits. (See Fig. 3, *b* below, and Fig. 6, *a* (page 55).)

Tracheides form the main bulk of wood, and therefore, of wood-pulp, especially in the case of conifers, in which the vessels are entirely absent. In distinction to the vessels, the tracheides are cells which are closed at both ends. According to the character of the thickenings of the cell walls, ringed cells, spiral cells, reticulated cells, ladder-form cells, and pitted cells are distinguished. (See Fig. 3.) The tracheides of coniferous trees show a spiral form of pit, the so-called bordered pits. Such borders are due to the fact that the thickened layer overlaps the thin cell wall where this is penetrated by the canal, but does not close entirely. Under the microscope one therefore observes the small circle of the aperture (the pit) surrounded by the larger circle of the overlapping thickened layer (the border). Apart from the pits the tracheides of pine wood often show broad, window-like openings, by which they may be distinguished from spruce. (See Fig. 6, *b*.)

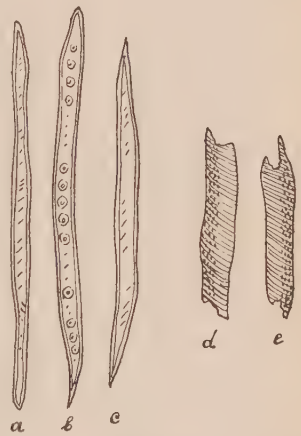


FIG. 3. PROSENCHYMA CELLS
a to *c*, tracheide fibres; *d* and *e*, vessel-like tracheides
Magnification: *a* to *c*, 15; *d* and *e*, 60

Vessels are produced when a number of aligned tracheides unite, with resorption of the transverse separating walls, forming tube-like structures, open at both ends. They then form continuous tubes which may attain a great length. The walls of vessels are always lignified. Their diameter varies from 0·05 to 0·6 mm. Like tracheides, vessels may be divided into ringed vessels, spiral, reticulated and pitted vessels, according to the

character of the wall thickenings. (See Fig. 7, *a*.) Vessels are found in the wood of deciduous trees, but not in that of conifers. (See Fig. 6.)

2. Parenchyma cells mainly serve, when alive, for the nutrition of the plant, that is, for its metabolism, and the storage of reserves of nourishment. They then contain living protoplasm, starch, and frequently also fatty materials (such as oils), resin and tannins. In the older woody tissues of trees they die out together with the prosenchyma cells. Parenchyma cells may either be of short spherical, polyhedric, or rectangular form, or may be longer, pointed at both ends, and rather like tracheides in shape. The walls of parenchyma cells are usually very thin but may be uniformly thickened, though in these cells local thickening in the form of rings, spirals, and so forth never occurs. Moreover, any pits which may occur are never bordered. The short parenchyma cells of wood are usually united to longer threads, which have the appearance of a single cell with transverse partitions. (Fig. 4, *b*.) The so-called pith rays (or medullary rays), which are more or less readily observable in many woods in transverse section, and which radiate from the pith to the bark, consist almost exclusively of parenchyma cells. Cells of this kind are usually destroyed relatively easily, therefore they are more easily destroyed by chemical action than the very resistant prosenchyma cells. They are, therefore, still to be found, along with the latter, in mechanical pulp, but are no longer present in completely disintegrated wood-pulp. (See Fig. 4.)

3. Sclerenchyma cells have usually a long, threadlike shape, pointed at both ends (see Fig. 5). Their walls are sometimes more or less strongly thickened, but uniformly so, as is the case with parenchyma cells, so that in this case also, ringed cells, spiral cells, and so forth, never occur. Pits are not common, and when they occur are extremely small and never bordered. Sclerenchyma cells occur more especially in the outer skin of plants ; in wood they serve to bind the woody fibres together and in older tissues they are usually strongly lignified or silicified. They never occur in the wood of conifers, but are found in that of deciduous trees.

The histological structure of cellulose fibres has already been described on pp. 26 and 27.

The Tissues. The cells of wood are agglomerated to form assemblages which develop as a whole, the tissues. These are described as prosenchyma tissue, parenchyma tissue, and so forth, according to the type of cells of which they are composed. A further distinction is made between formative tissue or meristem and permanent tissue. The former consists of cells

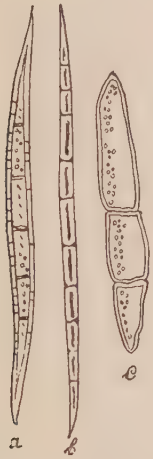


FIG. 4. PARENCHYMA CELLS
a, subdivided; *b*, chain of short cells; *c*, medulary parenchyma
Magnification 40

FIG. 5. SCLERENCHYMA CELLS
Magnification 50

which rapidly increase by division, as in the growing points of stems and roots and the cambium layer of trees, which is situated between the wood and the bast. On the other hand, the permanent tissue consists of fully grown cells, which have ceased to subdivide, more particularly the cells of the bark, the pith, sap-wood and heart-wood. Finally, the tissues are differentiated, according to the development of the tissue cells and the position which they occupy in the plant structure, into epidermis, ground tissue, and fibrovascular bundles. The epidermis consists mainly of rather small, thick-walled sclerenchyma cells. The ground tissue is the main mass of tissue,

surrounded by the epidermis, and consisting mainly of parenchyma cells. Finally, the fibrovascular bundles are the thread-like aggregates which are enclosed in the ground tissue in many plants, and are almost always composed of prosenchyma cells, but are, however, frequently interspersed with parenchyma tissue and usually run along the main direction of the organ in which they occur. The stem of a tree is in a sense a single fibrovascular bundle.

Chemical Constituents of Wood. As already mentioned, the cell walls consist of almost pure cellulose, with all the properties already described (see page 20 *et seq.*). But the cellulose in wood is not in the same condition of purity as that of cotton, for example. During lignification the cells which take part in that process cease to participate in the ordinary life process of the plant. Their protoplasm disappears and the physiological processes of metabolism, growth, and so forth, cease so far as they are concerned. They become rigid structures, which essentially serve to strengthen the body of the plant, as channels for the circulation of water and sap, and to some extent as storage for food supplies. During lignification their strength increases considerably, whilst they lose elasticity. These phenomena are primarily a consequence of the chemical combination of the cellulose, or impregnation of the cell wall, with the substance which is the real cause of lignification, namely lignin, a compound the chemical constitution of which has not yet been discovered, nor the manner of its formation or of its combination with the cellulosic component of wood. It contains hydroxyl, methoxyl and probably carboxyl groups, and also possibly acetyl residues. P. Klason considered lignin to be a condensation product of coniferyl and oxyconiferyl alcohols.

The quantities of these substances which could be isolated were, however, much too small to justify any conclusions on the structure of the whole molecule, or even on the main component of the same. The aromatic nature of lignin cannot be held to be proved. Regarding the formation of lignin, it is considered by some to be a product of the chemical transformation of cellulose ; others assume that it is produced

by added foreign substances. Lignocellulose is considered by some to be a true chemical compound, of the nature of an ester or an ether, whilst others assume that it is the product of a mere incrustation (intimate interpenetration) or adsorption of lignin by cellulose. The problem is too far removed from our main subject to be considered at length, and we will, therefore, restrict ourselves to a reference to the citations from the literature at the end of this book. The proportion of lignin (and, therefore, also the proportion of cellulose present) in wood, varies extremely for various woods. The soft woods contain less lignin and more cellulose, whilst in the hard woods the reverse is the case. Also, old wood contains more lignin than new wood. Hugo Müller gives the following figures, referred to dry wood, in Hofmann's *Report on the Vienna Exhibition of* 1873, Plant Fibre Section, page 150 (1877). Though their absolute reliability may be doubtful, they give a useful picture of the relationships—

Variety of Wood	Water per cent	Cellulose per cent	Incrusting matter per cent	Resin per cent
Birch	12·48	55·52	28·21	1·14
Beech	12·57	45·47	39·14	0·41
Box	12·90	48·14	35·70	0·63
Ebony	9·40	29·99	48·08	2·54
Oak	13·12	39·47	34·30	0·91
Alder	10·70	54·62	31·33	0·87
Lime	10·10	53·09	29·32	3·93
Chestnut	12·03	52·64	28·82	1·10
Pine	12·87	53·27	28·18	1·63
Mahogany	12·39	49·07	27·61	1·02
Black poplar	12·10	62·77	20·88	1·37
Fir	13·87	56·99	26·91	0·97
Willow	11·66	55·72	28·74	1·23

P. Klason gives the following average composition of spruce wood, which at present supplies by far the largest portion of the raw material for artificial silk manufacture (O. N. Witt, *Report on the International Congress of Applied Chemistry*, page 309). Cellulose, 53 to 55 per cent ; other hydrocarbons,

10 to 14 per cent ; lignin, 29 to 30 per cent ; resin, fat, and ash, 3·3 to 5 per cent ; proteins 0·7 per cent.

Lignin is well characterized by a number of reactions, which enable it to be readily detected in materials produced from wood, such as mechanical pulp, wood-pulp, paper and so forth. For example, there is the splendid red coloration with phloroglucinol and hydrochloric acid, first discovered by Wiesner, the intensive yellow coloration on treatment with moist chlorine, discovered by Cross and Bevan, and various other reactions. According to recent investigations, however, it appears uncertain whether these reactions are really due to lignin, or whether they are produced by substances by which it is always accompanied.

Apart from the main constituents of wood, cellulose and lignin, it almost always contains in addition hemicelluloses and pentosans, and also a whole series of the usual accessory plant materials, water, ash, tannins, dyestuffs and resins. They all possess a certain interest for us here, as none of them is quite completely removed during the isolation of cellulose, so that the remains of these substances are usually present in wood pulp, although they must not exceed a certain proportion if they are not to interfere with the process of artificial silk manufacture.

The hemicelluloses are polysaccharides which are intermediate in chemical character between cellulose and starch, and may, therefore, act as structural elements, like cellulose, or as reserve materials, like starch. They are much more readily hydrolized by dilute acids than cellulose. The hemicelluloses of wood, which alone interest us here, are always hydrolized by the reagents employed to separate them from lignin and so forth, so that it has not yet been found possible to isolate them in a pure form. As the products of their hydrolysis are mainly mannose and galactose, they evidently consist of mannans and galactans. Apart from the fact, already referred to, that they are readily decomposed by dilute acids, they are readily distinguished from cellulose by the fact that they are destroyed by heating to 300° C. in glycerine. Some hemicelluloses are dissolved at the ordinary temperature

by sodium hydroxide solution of about 5 per cent concentration, whilst others only dissolve on warming. They are reprecipitated from such solutions by acids, or better by acids and alcohol. With iodine and sulphuric acid or iodine and zinc chloride solution these precipitates give the colorations which characterize carbohydrates of the cellulose group.

These properties are more or less completely shown by the pentosans of wood, which have, therefore, been included by some investigators in the hemicelluloses. But this is an error. The pentosans form a parallel class to the hexosans (cellulose, starch, and so forth) and their relations to the pentoses are the same as those of cellulose to glucose. The most important pentosan of wood is xylan, which is readily hydrolized by dilute acids to xylose, or wood sugar, of the formula $C_5H_{10}O_5$. Its isomer, araban, which yields arabit on hydrolysis, also occurs in variable, very small, quantities; methyl-pentosans also accompany the pentosans. The cherry red coloration of the liquid obtained when wood is boiled with dilute hydrochloric acid in presence of phloroglucinol is due to the presence of pentosans.

On distilling with hydrochloric acid of about 12 per cent strength furfurol is apparently obtained (and methyl-furfurol from methyl-pentosans) which is readily identified by the intensive red coloration obtained with aniline acetate and which can be quantitatively determined as furfurol phloroglucide. The crude mixture of pentosans which is extracted from wood or wood-pulp by alkalis and reprecipitated from the alkaline solution by acids and alcohol, is ordinarily

	Methyl-pentosan per cent	Pentosan per cent
Oak wood, 18-year trunk	2·26	19·06
,, ,, younger trunk	2·31	18·60
,, bark, 18-year trunk	2·08	14·21
,, ,, from young branches	2·54	12·85
Cedar wood	2·90	12·36
Spruce ,,	4·70	10·03
Birch ,,	2·68	23·59
Ash ,,	2·95	17·24

called wood gum. It was first obtained by Poumarede and Figuier from poplar wood and beech wood. (*Comptes Rendus*, 1846, Vol. 23, page 916.)

The pentosan contents usually increase with the age of the wood. They vary greatly, however, with the nature of the wood, and more especially are usually much higher in wood from deciduous trees than in wood from conifers. For example, Sebelien published the figures given at the foot of page 39. (*Chem. Ztg.*, 1906, page 401.)

Water Contents. The water contained in wood is present to a varying extent, amounting on the average to about one-half, in the liquid form, whilst the remainder is absorbed in the cellular tissue in the form of " water of imbibition." The total quantity naturally varies greatly, being dependent on a large number of factors, such as the age of the tree, the locality, the season and so forth. The sap wood usually contains much more water than the heart wood, and wood felled in winter considerably less than that felled in spring. The amount of water in newly felled wood varies from about 20 to about 50 per cent. Air dried wood (after about two years' storage) usually contains about 10 to 20 per cent of water. The proportion of water in sap wood may be three times the quantity in the heart wood, and may amount to 65 per cent and more. Floated wood naturally contains a relatively large amount of water, being about 60 per cent on the average.

Ash Contents. The amount of ash, that is, of non-combustible material, mostly salts, which remains behind on burning, also varies greatly in various woods. It varies according to the kind of wood, its age, locality of growth, nature of soil, season and part of the tree from which the sample is taken. Woods from deciduous trees usually contain more ash than those from conifers. Where active growth occurs, resulting in a more ample supply of sap, containing salts in solution, a larger proportion of ash is found in the wood. Thus, more is found in young than in old wood, more in sap wood than in heart wood, more in the branches and twigs than in the stem, and more in spring than at other seasons. The total ash contents are usually less than 1 per cent of the dry solid of the wood

and seldom amount to 3 to 4 per cent in woods exceptionally rich in ash, whilst in woods containing especially little ash, the ash contents may be as low as about 0·2 per cent.

Lime is almost always the predominant constituent of wood ashes. In varieties rich in lime, especially in the woods of deciduous trees, the lime often amounts to two-thirds to three-quarters of the total ash, whilst in varieties poor in lime, such, for example, the spruce (*Picea excelsa*), the ash contains barely 30 per cent CaO, and the ash of the silver fir (*Abies pectinata*) only 10 per cent. The lime contents are partially due to calcium salts of organic acids, which are only converted into $CaCO_3$ on incineration. Lime is, however, also found in wood, to a greater or less extent, as deposits of crystalline $CaCO_3$, especially in the tracheides and parenchyma cells of the heart wood, in which it plays a part as a structural element in the conversion of sap wood into heart wood. The second most abundant constituent of wood ash is usually *potash*, which may even exceed the lime in amount in plants containing comparatively little of the latter. The average values are usually 10 to 20 per cent K_2O, calculated on the total ash. In woods rich in potash it may be as high as about 45 per cent, whilst in woods especially deficient in potash it may be less than 10 per cent. Potash is essentially a constituent of the sap and is present in the form of soluble organic and inorganic compounds, so that from spruce wood, for example, about 75 per cent of the total potash can be extracted by water. The *soda* contents of wood are usually very low. In exceptional cases they may amount to 10 to 15 per cent Na_2O in the ash, usually, however, they amount to about 0·5 to 2 per cent only. Soda can only be extracted from wood by water with difficulty or to a very small extent. *Magnesium* is an important constituent of all green plants, as it is a constituent of chlorophyll, as was first shown by Willstätter. Apart from extreme cases, wood ash contains from 5 to 10 per cent of MgO. In the ash from the wood of the spruce and the silver fir it amounts to about 6·5 per cent according to G. Councler (*Just's Botan. Jahresber.* (1886) I, page 161). Schroeder, on the other hand, gives a very much higher value, namely, more than 13 per cent (see Czapek,

Biochemie der Pflanzen, 1920, II, page 409). He found the following percentages of MgO in the pure ash of spruce wood at various seasons—

	April	August	November	February
From outer wood . .	10·44	7·89	9·37	9·47
From inner wood . .	13·07	14·94	12·77	13·40

He was only able to extract a relatively small proportion of magnesium from spruce wood by water. *Alumina* and *manganese oxide* are not present in all woods. Whilst neither substance usually exceeds 0·5 to 0·9 per cent of the total ash, they occasionally occur in considerably greater quantity, especially in the wood of conifers. This is especially true of manganese oxide. Thus, Schroeder found over 40 per cent Mn_3O_4 in the ash of the silver fir and more than 22 per cent in that of the spruce. According to Guérin (see Czapek, *Biochemie der Pflanzen*, 1920, page 410), these woods contain manganese-bearing nucleinic acids, which can be extracted with potassium hydroxide solution and reprecipitated by gentle acidification. The *iron* contents of wood usually amount to 0·5 to 0·8 per cent of the ash, but occasionally amount to several per cent. Only a very small amount of the iron is present in water-soluble form. Schroeder found 6·33 per cent of iron oxide in the ash of non-extracted spruce wood, 7·38 per cent in that of the extracted wood and 2·38 per cent in the ash from the aqueous extract.

Phosphoric acid is almost always present in woods, but the amount varies very greatly, more particularly with the amount of phosphate in the soil. The ash usually contains 3 to 4 per cent of P_2O_5 only, but this frequently rises to about 10 per cent. In a considerable number of cases, however, 20 per cent and more P_2O_5 was found in the ash. The remarks made above with regard to the quantity of ash in general are particularly applicable to the phosphoric acid contents. These are particularly high in cases where growth is active and where, consequently, there is an abundant circulation of sap containing

salts in solution. According to Schroeder's results (see Czapek, *loc. cit.*, page 411), a very small amount only of the phosphoric acid in spruce wood can be extracted with water. The ash of the unextracted wood contained 1·30 per cent, P_2O_5, that of the extracted wood 1·01 per cent, and that of the extraction residue 1·41 per cent. Here and there phosphoric acid could be identified in the wood cells in the form of deposited calcium phosphate. The *sulphur* contents of wood ashes are small and very seldom exceed 4 per cent of the ash. The form in which the sulphur is present has not yet been satisfactorily decided. Schroeder was only able to extract very small quantities of sulphur compounds from spruce wood with water. The sap wood always seems to contain rather more sulphur than the heart wood, and it is not impossible that the albumen contents of the living cells play an essential part in this matter. *Silica* is present in all wood ashes, though in very varying amounts. It usually amounts to 1 to 3 per cent of the total ash, but woods exist which are very rich in silica, the ash of which may contain 30 per cent SiO_2 and more. The spruce is one of this class, and 36·18 per cent SiO_2 has been found in the ash of this tree. Silica is always more abundant in older, strongly lignified parts of trees than in younger portions which are still growing, in contrast to the distribution of most other ash constituents, so that, for example, heart wood usually contains considerably more silica than sap wood, the lower portions of the trunk more than the upper portions and so forth. Finally, the *chlorine* contents of wood ash must be mentioned, though with a few exceptions it is only present in traces or in very small quantities, amounting at most to 2 to 3 per cent of the ash. *Tannins* and *dyes* do not occur in serious quantity in the varieties of wood with which we are here concerned. The formation of so-called "red wood" in fir wood and oak wood is possibly due to the oxidation of very small quantities of tannins.

Production of Wood-pulp. In order to be able to utilize the cellulose of wood for artificial silk manufacture it must be isolated, a process the rational operation of which is the main problem of the wood-pulp industry. The ideal solution of this

problem would be the isolation of wood cellulose with both the chemical purity characteristic of cotton and in the form of entirely intact and sound fibres. As usual, this ideal is not achieved in practice. The separation of wood cellulose from the encrusting materials requires such energetic chemical action, which is not without effect on the cellulose fibre, that this would be too severely attacked if its separation from all impurities were carried to an extreme.

The production of wood-pulp is always carried out by boiling the disintegrated wood with certain chemicals under high pressure. According to the character of the chemical reagents one distinguishes alkaline and acid processes. The former produce soda and sulphate pulp and the latter sulphite pulp.

Historical. Both the above-mentioned processes originated in America. About 70 years ago, in 1854, the same year in which Charles Mellier, of Paris, patented his process of disintegrating straw with caustic soda solution in France, the Englishmen, Charles Watt and Hugh Burgess, obtained their first American patent for the manufacture of cellulose by alkaline treatment of wood. This patent, together with a few succeeding patents, was taken over by the Americans, Ladd and Keen, and was first operated (prior to 1860) at Royersford, Pennsylvania. The success of the process led to the formation of The American Wood Paper Co., with large works at Manayunk, near Philadelphia. At about the same time (1857) the British manufacturer, Houghton, decomposed straw by the same methods. The regular manufacture of cellulose by his process was carried out in the Cone Mills works, near Sidney, Gloucestershire, which were erected in 1866, and later in an engineering works under the management of James A. Lee in Derby, which constructed many installations in all parts of Europe in the 'seventies. The process of Sinclair, which was evolved at about the same period, and which was also introduced into many European works, was chemically identical, but differed in the arrangement of the boilers and evaporators. Houghton's process was operated by the first German wood pulp works of Max Dresel, of Dalbke, near Bielefeld, in 1873. The other alkaline process, the sulphate process, in which a

portion of the caustic soda is replaced by sodium sulphide, produced from added sodium sulphate during the calcination of the evaporated liquors, was invented by the engineer, C. F. Dahl, of Danzig, in the year 1884.

The development of the acid wood-pulp process was almost simultaneous with that of the soda process. Its first beginnings are to be found in an American patent, dated 1851, of the Englishman, P. Clausen, who described the recovery of straw cellulose by the action of SO_2 on straw soaked in alkali. The disintegration of wood and other vegetable tissues by the action of SO_2, alone or together with a base, is described in French patent 116,996, of 1877, by the French paper manufacturer Lioud, of Bourg-Argental. The first manufacturing attempts were, however, carried out by the chemist, Benjamin Tilghman, of Philadelphia, partly in conjunction with his brother, Richard, in the years 1866 to 1869, in the Harding Paper and Pulp Mill at Manayunk, near Philadelphia. The experiments were carried out with much perseverance for years, but did not lead to large manufacturing developments, as they had finally to be abandoned, partly owing to adverse conditions and partly no doubt, on account of plant difficulties, which had not yet been overcome.

In Sweden, C. D. Ekman had already produced sulphite pulp since the year 1874. He used magnesium bisulphite as a disintegrating agent, and kept his process secret for a long time. The first (Luxemburg) patent of Professor A. Mitscherlich dates from the same year, 1874. It is due to Professor Mitscherlich that the sulphite process, the principles of which were already known through the Tilghman patents, was not only widely introduced, but was also so excellently developed from the plant standpoint that it is still carried out by his methods, with but few alterations. Dr. Karl Kellner independently discovered the disintegration of wood by calcium bisulphite in the middle 'seventies, and developed his process practically in the years 1878 to 1879 in the paper mills of Baron Ritter, at Podgora, Austria. He boiled with direct steam, but otherwise his process, commonly known as the Ritter-Kellner process, differs but little from the Mitscherlich process.

Soda Pulp and Sulphate Pulp. These have not so far been used for artificial silk manufacture, and are, therefore, of but little interest to us here. As it is not, however, impossible that they may one day be produced by modified processes and used for the purpose, we will give a short sketch of their manufacture.

All classes of wood can be disintegrated by these processes, and also grasses, straws, and so forth. Also, they are able to deal more particularly with woods rich in resin, for example, pine wood, which cannot be treated by the sulphite process. The materials preferred for these processes are pine, spruce, and aspen wood. The concentration of the liquor, pressure, and temperature during the boiling process, and its duration, depend entirely on the character of the raw material and the degree of disintegration required.

According to the simple soda process, for example, a liquor containing 6 to 8 per cent of NaOH may be used. The wood, in chips about 2 to 3 cm. long, is boiled in the liquor for 5 to 8 hours at 160 to 180° C., corresponding to a pressure of 6 to 8 atmospheres, the weight of liquor being about four times that of the wood. According to Christiansen (*Ueber Natronzellstoff*, Berlin, 1913), the decomposition of the lignin commences at above 150° C., and soda pulp is only completely separated from lignin if boiled at temperatures of 170 to 175° C. The digesters are large cylindrical iron vessels of 70 cu. m. capacity and over, which may be either vertical or horizontal and are constructed of strong boiler plate, which may be either riveted or welded. They are sometimes arranged to revolve about a horizontal axis in order to enable the contents to be well mixed by occasionally revolving the boiler slowly, in which way their uniform treatment is promoted. Heating is usually effected by direct steam, more rarely by indirect steam.

After the conclusion of the boil the pressure is released, either completely or until the so-called blow-off pressure is attained. In the case of woods containing much resin, considerable quantities of turpentine escape with the steam and may be recovered by condensation. From 1 ton of pine wood, for example, 10 to 12 kg. of turpentine are obtained. After running

off the liquor the cellulose is either washed with as little water as possible in the boiler itself, or, more usually, is blown out into an iron washing tank with drainer bottom in order to save time for the next boil. In this the material is extracted with as little water as possible. In some works, several (3 to 4) diffusers are connected in series and the product is washed in these on the counter-current principle. Every endeavour is made to obtain the strong liquors and washings in as concentrated a form as possible, as these have to be evaporated in order to recover the valuable alkali. The washed product is either used directly for other manufactures or is dried in the form of sheets and so marketed. By the simple soda process the yield is seldom more than 35 per cent of the wood which is treated.

In order to recover the alkali, the liquors are first concentrated to 30 to 40° Bé in vacuum pans or tray evaporators, and are then further evaporated in rotary driers, such as are used in the alkali industry, to a syrup, which is finally incinerated in a furnace until the whole of the organic matter or carbon has been burnt. The molten mass is dissolved in water and causticized with quick-lime. After separating from the calcium carbonate sludge and replacing the loss of caustic soda, which amounts to about 10 to 15 per cent of that originally employed, the liquor is once more ready for use. Instead of adding caustic soda, sodium carbonate can, of course, be added before the causticizing process.

The principle of the other alkaline process, the sulphate process, consists in the addition of sodium sulphate to the evaporated recovered liquor before melting. This sodium sulphate is reduced to sulphide by the carbon formed from the organic matter during the incineration and ignition process. The sodium sulphide, being a weak alkali, assists in the disintegration of the wood, although to a lesser extent than the caustic soda. Further, during the causticizing process, a portion of the Na_2S is converted into NaOH and CaS, which latter is eliminated with the calcium carbonate sludge. The regenerated liquor still contains 2 to 3 per cent Na_2S, 7 to 8 per cent NaOH, 3 to 4 per cent Na_2CO_3 and 2 per cent Na_2SO_4. The consumption

of sulphate varies from about 15 to 25 kg. per 100 kg. of cellulose. The yield of cellulose is considerably higher by this process than by the simple soda process, and amounts to about 40 to 48 per cent of the wood treated. A great disadvantage of this process consists in the terrible odours caused by the organic sulphur compounds, mainly methyl mercaptan and methyl sulphide, which escape with the flue gases, and which render the neighbourhood of sulphate pulp works so intolerable as to prevent its widespread adoption. Many methods of avoiding these smells have been proposed, but none of these has so far been practically successful.

Sulphite Pulp. In the sulphite pulp process the wood is decomposed by an aqueous solution of acid calcium sulphite, or sometimes of acid magnesium sulphite, in presence of an excess of sulphurous acid. Sodium sulphite is also used, though only occasionally. These compounds possess the property of removing the lignin from the cellulose by solution at high temperatures, apparently with formation of lignin-sulphonic acids or their salts. Little is known of the character of the reaction, for, as already explained (page 36), the constitution of the lignin molecule and the nature of its union with the cellulose molecule are still quite unknown. Possibly combination is due to the aldehyde groups, although it may be due to interaction with ethylenic double bonds which are dissociated during the process.

The sulphite liquor is usually prepared in large wooden towers in which water trickles down over limestone, whilst cooled, washed pyrites burner gases pass upward from below. The sulphur dioxide in these gases decomposes the calcium carbonate with formation of bisulphite, which dissolves in the water. At the tops of the towers carbon dioxide escapes, mixed with air and water vapour only. The discharged tower liquor contains on the average about 2·5 to 3 per cent of SO_2, but is usually reinforced by the acid waste gases evolved from the boiled batches. The composition of the bisulphite liquor varies according to the boiling process adopted, as the digesters may be heated indirectly or by direct steam. In the latter case the liquors are naturally much diluted by condensed steam.

and must, therefore, have a greater initial concentration. The lime contents do not usually differ much in the two cases and usually correspond to about 1 per cent CaO, but rather more in the Ritter-Kellner form of the process, although never more than about 1·5 per cent CaO. For indirect boils (Mitscherlich boils) the liquors contain about 2·8 to 3 per cent total SO_2, of which 1·5 to 1·8 per cent is in the form of free acid. In the boiling processes with direct steam (Ritter-Kellner boils) liquors are used containing 4 to 5 per cent of total SO_2, of which about 3 to 3·5 per cent is in the form of free acid. Latterly, much more concentrated solutions have sometimes been used for purposes of economy, containing up to 7 per cent of SO_2. According to Klason (*Bericht d. Ver. d. Zellstoff-u. Papier-Chem.*, 1909, page 61) the theoretical requirements are 76 parts SO_2 and 32 parts CaO per 1,000 parts of wood, according to which, on the assumption of 0·5 cu. m. of liquor per 100 kg. of wood, the minimum concentration of the liquor would be only 1·6 per cent of SO_2 and 0·7 per cent of CaO. The free acid should amount to about 70 per cent of the total acid.

In our description of the historical development of the sulphite process we have already explained what is meant by the terms " Mitscherlich boil " and " Ritter-Kellner boil." It is not, however, necessary to use one or the other process alone, that is, to boil with either indirect or direct steam. On the contrary, the two methods of boiling are frequently united in various forms. As there are considerable differences between the two systems with regard to pressure, temperature, and duration of the boil, the method of boiling exercises a considerable influence on the character of the pulp. The Ritter-Kellner process supplies soft, not very tough, rather cotton-like pulp, which is usually very easily bleached, whilst Mitscherlich pulps are hard and tough, have rather the character of bast fibres (linen) and are usually not so easily bleached as Ritter-Kellner pulps.

Sulphite boils are carried out in enormous digesters, frequently of several hundred cubic metres capacity, which are usually vertical and constructed of riveted boiler plates, and are coated within with acid-proof tiles as a protection against

the action of the sulphurous acid. In some works the boilers are lined with lead only, whilst in other cases a lead lining is used which is in turn coated with acid-proof tiles.

As in the soda and sulphate processes, the wood is used in the form of chips which are 2 to 3 cm. long. In the case of the Mitscherlich process especially, the wood is often steamed for a few hours in the digester before the addition of the liquor, in order to remove air from its pores and to facilitate the penetration of the liquor. The actual boiling is usually carried out in several stages. After heating up to about 110° C. and a corresponding pressure of 2 to 3 atmospheres, the steam supply is cut off for some hours, during which period uniform penetration of the wood by the liquor occurs. The full boil then takes place and is followed, after a further pause, by the finishing boil. By the Mitscherlich process a long boil is given (35 to 40 hours and over) at a relatively low temperature of about 135° C., and 3 to 4 atmospheres pressure, whilst by the Ritter-Kellner process the boil is carried out at 140 to 150° C. and 4 to 6 atmospheres of pressure, which enables the boil to be completed in 9 to 15 hours. The pressure during the boil is controlled by occasionally blowing off the gases. The sulphur dioxide which escapes is utilized, as already mentioned, for increasing the acidity of the fresh liquors from the absorption towers.

The boils are controlled, especially towards the end of the operation, by repeatedly drawing samples of the liquor from a sampling cock with which the digester is provided and testing these. The condition and completion of the boil are judged from the colour, smell, taste, and stickiness of the liquor, and more especially from the contents of sulphur dioxide. The so-called Mitscherlich test is also still much used. This enables conclusions to be drawn regarding the stage which the process has reached from the amount of calcium monosulphite precipitated from the liquor on adding ammonia. The amount of this precipitate from a given quantity of liquor decreases gradually during the boil, and experience shows that the operation is complete when it finally attains a minimum.

After the completion of the boil the batch is blown off, that is, the pressure is reduced until it is quite small. The sulphur

dioxide which escapes during this operation may also be used to strengthen the fresh tower liquors. Various methods are adopted for emptying the contents of the digester. Usually, after blowing off, the liquor is withdrawn and cold water is sprayed into the digester; this causes cooling, condensation, and absorption of the gases and vapours in the digester, resulting in the complete disappearance of the excess pressure, or even the production of a slight vacuum. The upper cover is then removed and the pulp is washed a few times in the digester, by alternately filling up with water and discharging it below. Finally, the lower lid of the digester is opened and the pulp emptied out by hand with shovels. In some works it is flushed out with water, into the pulp boxes, either with the first wash water, in which case it is washed completely in the pulp box, or with the last wash-water, in which case it is merely drained in the pulp box. Some works prefer to blow off only until 1 or 2 atmospheres excess pressure remain in the digester, and to utilize the remaining pressure to evacuate the contents through a wide pipe at the bottom of the digester and into large bins provided with sieve floors. In these bins the pulp is first separated from the liquor and then washed, after which it is conveyed to the remaining purifying plant.

Twigs, bark residues, and so forth, which are usually completely disintegrated by the soda process, are almost unattacked by the sulphite process, and must, therefore, be carefully removed from sulphite pulp by twig and knot catchers.

The yield of cellulose by the sulphite process varies within somewhat wide limits according to the variety of wood, the conduct of the boiling operation, purity of the pulp and so forth, and is about 38 to 45 per cent of the wood treated. According to Harpf (*Zts. f. angew. Chemie*, 1898, Part 38), about 37 per cent of the sulphur dioxide used in the boil can easily be recovered. According to Kirchner (*Das Papier*, page 346), more than 47 per cent of SO_2 has already been recovered.

V. Possanner (*Chem. Technologie des Papiers*, 1923, page

143) gives the following consumption of materials for the production of 100 kg. of sulphite pulp—

	kg.
Wood, 0·65 gross cu. m. = 0·45 cu. m. =	200
Sulphur	10–15
Limestone	15–20
Coal for power	30–40
„ boiling	40–60
„ drying	20–40
„ (total)	100–200

Sulphite Waste Liquors. About 1,000 litres of waste liquors are obtained per 100 kg. of sulphite pulp. These were formerly rejected as a valueless by-product. They are now utilized to a considerable extent. They contain about 1 to 1·5 per cent of fermentable sugar, which is fermented and supplies the so-called sulphite alcohol to the amount of 5 to 6 litres per cu. m. of liquor. After being more or less purified, for example, after removal of the lime, the waste liquors are evaporated to various concentrations and then find sundry applications under the name of cellulose extract. In consequence of the organic colloids which they contain, which possess both adhesive and tanning properties, they can be used as cheap adhesives, as additions to tan liquors, as dust fixing agents and for other similar purposes.

The Bleaching of Wood-pulp. Sulphite pulps are usually easily bleached, whilst soda and sulphate pulps usually bleach with difficulty, and are sometimes unbleachable.

The bleaching materials ordinarily used are calcium or sodium hypochlorite solutions, which are produced in the well-known manner by passing chlorine into milk of lime or sodium hydroxide solution, or, in the latter case, more directly by electrolytic decomposition of brine in the absence of a diaphragm. Sodium hypochlorite solutions may also be prepared by interaction of bleaching powder suspensions and sodium carbonate.

Wood-pulp is usually bleached in large kiers (hollanders) in which the pulp suspension, which is usually of 6 to 8 per cent strength, is slowly circulated by propellers. The bleaching liquid contains 0·3 to 0·5 per cent of active chlorine or a corresponding concentration of hypochlorite (for example, 1 per

cent of bleaching powder). The consumption of chlorine naturally varies greatly with the purity of the material to be bleached, the degree of bleaching to be attained, and so forth. The minimum consumption of bleaching powder might be estimated at about 5 per cent and the maximum at 25 per cent of the weight of cellulose.

The bleaching process acts in two directions. Colouring matters are destroyed, undesired coloration of the pulp removed and a more or less completely white appearance attained according to requirements, whilst on the other hand, any lignin residues and other encrusting constituents are oxidized and the decomposition of the wood fibre thus completed. This removal of undesired impurities is, of course, accompanied by loss of weight, which may vary within rather wide limits according to the proportion of impurities in the unbleached material, and the degree of whiteness and completion of the oxidizing process which it is desired to achieve. On the average, a loss of about 5 to 10 per cent of the cellulose may be anticipated.

At raised temperatures the bleaching process proceeds much more rapidly, but is under certain circumstances accompanied by marked weakening of the fibre in consequence of oxidation of the cellulose. At raised temperatures chlorate is also more readily formed and, being inactive, represents a loss of active chlorine. For these reasons, high temperatures of more than 40° C., for example, are better avoided, even in cases where cold bleaching is not preferred. When bleaching is too intensive, considerable amounts of oxycellulose are formed, and, under certain circumstances, and in presence of acid, even hydrocellulose. In this way the pure alphacellulose contents of the pulp are reduced and the fibre is more or less weakened.

After bleaching, the pulp is very carefully washed. This is necessary, both because the ash contents are otherwise too high and because imperfectly washed pulp more easily alters in character on storage and tends to become yellow. Bleached pulp is dried in the same manner as paper, by dehydration on a Foudrinier machine, and drying on the steam heated drying cylinder equipment of such a machine.

In German patent 337,725, G. A. Krause proposes to expose

the wet cellulose, whilst in a finely dispersed condition, to the action of a current of warm air. The process did not prove successful in practice.

Properties of Wood-pulp. If we bear in mind that the dry solids in wood-pulp usually contain about 90 per cent of cellulose, it will be evident that from the chemical standpoint the behaviour of wood-pulp will correspond, in the main, to that of cellulose, as described on page 20 *et seq.* But the method and operation of the whole manufacturing process often lead to quite considerable variations in the properties of the various varieties of wood-pulp, partly due to the cellulose fibre itself, and partly to the admixed impurities.

The extent to which the cellulose fibre in wood-pulp is affected by the process of manufacture was partially explained during the description of the various processes which it undergoes. The fact is worth special attention that the conditions during the acid process are more favourable to the ultimate production of cellulose solutions than are those which occur during the alkaline process. This may be due to some unfavourable chemical action of the caustic alkali on the cellulose at high temperatures, which alters it in a manner prejudicial to its solution, or to some action of the acid on the cellulose during the acid process (depolymerization or the like), or perhaps to both these causes. In any case, the practical result is that, as already indicated, sulphite pulps only have so far proved suitable for the manufacture of artificial silk, whilst soda and sulphate pulps have not. If, for example, the conversion of the last named material into viscose is attempted, it is found that the fibres react very unevenly and the solution, therefore, contains a large number of fibres which have reacted either slightly or not at all, that the liquid is viscous and difficult to filter, and that in short, no utilizable viscose solution is obtained. Regarding wood-pulp fibres, see page 32 *et seq.* and also Figs. 6 and 7.

Impurities in Wood-pulp. The amount of moisture in wood-pulp corresponds to the hygroscopic properties of cellulose and averages 8 to 12 per cent. Wood-pulps also contain more or less

considerable quantities of impurities, partly derived from the wood and partly from the various materials used in its treatment. These are more particularly resinous and fatty substances, hemicelluloses and pentosans (wood gum), lignin residues and ash, which have all been previously discussed in detail in the earlier section on the chemical constituents of wood (page 36 *et seq.*). The ash components in particular may be derived to a varying extent from the reagents used during manufacture, more particularly alkali and alkaline earth salts

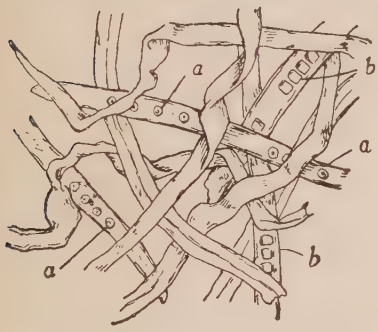


Fig. 6. Coniferous Wood Fibre
Magnification 100

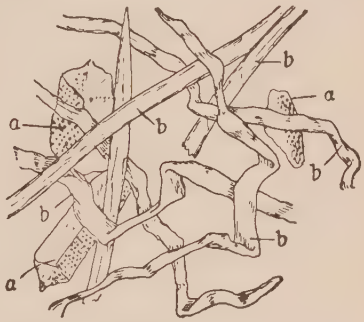


Fig. 7. Deciduous Wood Fibre
Magnification 100

from the boiling liquors, wash-waters, bleach solutions, and so forth.

The question whether or not a wood-pulp is suitable for a given artificial silk process cannot be decided with certainty on the basis of a chemical analysis alone. A very large number of factors is involved, and the relation between each of these and the artificial silk process is as yet by no means clear. Further, the methods adopted in the various artificial silk works, even though they may manufacture the same type of artificial silk, often vary greatly, and cases occur in which a wood-pulp cannot be utilized by one works, but is utilized by others with great success. Finally, the physical properties of the wood-pulp exercise an effect which should not be underestimated on its conversion into artificial silk.

In spite of these considerations, chemical analysis supplies

certain particulars and useful indications, and usually enables a decision to be arrived at as to whether a particular wood-pulp may be discarded as unsuitable without further investigation, or whether its utilization appears possible. For example, no works could satisfactorily convert into artificial silk a wood-pulp which was found to contain 75 per cent of alpha-cellulose and gave a copper value of 6 to 7. Generally speaking, the following analytical figures may be considered as normal for a wood-pulp especially suitable for artificial silk manufacture: alpha-cellulose, 85 to 90 per cent; hemicellulose, 11 to 14 per cent; ash, 0·15 to 0·3 per cent; resin (soluble in ether), 0·6 to 0·7 per cent; copper value, 2 to 3.

Most of the wood-pulps for artificial silk manufacture at present placed on the market by various firms conform to these requirements. As an example of such materials we may mention the special quality of wood-pulp for artificial silk manufacture supplied by Zellstoffabrik Waldhof (Mannheim-Waldhof), further details about which as a raw material for viscose silk, are given on page 261.

As already mentioned, the physical properties of wood-pulp also exercise a certain influence on its use for artificial silk manufacture. The wood-pulp must have good absorptive properties, in order that it may absorb the chemicals, with which it is treated in the process of artificial silk manufacture, in a satisfactory and uniform manner. In order to produce a good fibre, the solution prepared from the pulp must have a certain viscosity, which must not exceed a definite limit, as otherwise difficulties would occur in the filtration of the solutions and their passage through the spinning nozzles. Moreover, if the solutions are too viscous it is usually impossible to draw the thread rapidly. The less the cellulose fibre has been attacked, the greater is the viscosity of its solution. Cellulose molecules which have undergone much degradation, for example, by hydrolysis, oxidation, and so forth, form thin, non-viscous solutions, which in turn yield poor threads. The viscosity of cellulose solutions, and also of solutions of other chemical compounds, affords a means of recognition of the size of the molecule.

OTHER CELLULOSIC MATERIALS

Apart from cotton and the wood of trees, cellulosic material from various other plants has been proposed or even tried, at least experimentally, for artificial silk manufacture. For example, in German patent 56,331, Chardonnet mentions straw, hemp, and ramie. Other cellulosic materials which have been suggested for the manufacture of collodium silk in particular are: Maize stalks (U.S. patent 845,378); broom (French patent 347,353); cotton seed capsules (German patents 171,604, 178,308, 183,923, 192,690, 196,677, 212,183). As a special material for the production of cuprammonium silk, Müller and Wolf, in German patent 256,351, propose the use of the fibre of hop-stems and similar plants. As a raw material for artificial silk in general H. Davoine, in French patent 470,606, proposes the cellulose obtained from *Hedychium coronarium*, a member of the family of the Zingiberaceae, which, according to him, is particularly suited to the purpose. It is said to produce an excellent artificial silk which is cheaper than other silks.

In British patent 12,422/1910, M. Weertz proposes the use of so-called vegetable silks (kapok fibre, bombyx fibre, and others) as a raw material. The fibres are first to be freed from oil and bleached, like cotton, and are then to be dissolved in the usual cellulose solvents and spun.

In spite of all these experiments and proposals, cotton and wood have so far remained the only raw materials used for artificial silk manufacture. With the present large production of artificial silk, a main requirement for any raw material is that it should be available in practically limitless quantities, which is the case for cotton and wood, but not for the other raw materials which have been proposed.

NON-CELLULOSIC RAW MATERIALS

It was but natural that materials other than cellulose or its derivatives should be tried for artificial silk production. We find, more particularly, that a large number of inventors were obsessed by the notion that the best artificial silk should

correspond in its chemical nature to natural silk, and should, therefore, be produced from a material which was chemically closely allied to fibroin. This idea led to the use of various materials of animal origin. But a whole series of the most various products of the vegetable kingdom were also tried, in so far as they possessed properties which enabled them to be formed into coherent threads under suitable conditions. Although none of these attempts resulted in continued success, we will deal with them after describing the manufacture of artificial silks from cellulose, and we will therefore deal briefly here with the properties of the raw materials which have been proposed for the purpose.

Agar-Agar, Chinese or Japanese gelatine, also known as Japanese or Bengal isinglass, is mainly produced in China and Japan from sea algae, by extracting with boiling water and pouring the extract into cold water. This is usually marketed in the form of long, narrow, more or less crinkled, colourless, transparent, very light rods or ribbons. It is produced from a whole series of plants, including *Gelidium Amansii*, *G. corneum*, *G. cartilagineum*, *Glocopeltis tenax*, *Gradeloupia filicina*, *Fucus amylaceus*, *Gracilaria lichenoides*, *Alga spinosa*, and others. The product is often designated according to its origin as Ceylon moss, Macassar agar-agar, Java agar-agar, and so forth. It contains no nitrogen and is less easily decomposed than gelatine. The jelly prepared from it is odourless and does not readily putrify. Its gelatinizing qualities are greater than those of gelatine. A $\frac{1}{2}$ per cent solution forms a jelly as stiff as that from a 3 to 5 per cent gelatine solution. The jelly-forming substance, also known as gelose, is a carbohydrate.

Albumen, or white of egg, is obtained from hens' eggs, which should be as fresh as possible, sometimes also from goose or duck eggs (egg albumen), or from the blood of animals (blood albumen). The white of egg is carefully freed from yolk and yolk residues, then neutralized with ammonia and evaporated to dryness in flat porcelain dishes at a temperature of less than 35° C. in order to avoid coagulation. In order to prepare blood albumen the blood is allowed to coagulate in zinc vats, and after removing the clots the serum is evaporated at a low temperature as in the case of egg albumen. Evaporation may be preceded by treatment with a little acetic acid and turpentine. Albumen from white of egg is a yellowish, very crumbly, almost odourless material of faintly alkaline reaction, which dissolves in water to form a turbid solution. Blood albumen is darker in colour, being red or brown. The quality of the product is usually judged by the solubility in water, the property of coagulating at 75° C., and of being precipitated by tanning materials.

Algin, or alginic acid, is an albumenoid substance, obtained from certain marine algae, which is used as a dressing for textiles, in the manufacture of photographic paper, and for other purposes.

Fibrin is the name of the proteid which separates in the form of threads when blood is beaten.

Fibroin is the nitrogenous albumenoid constituent of natural silk.

Gelose. (See Agar-Agar.)

Glutin and Glutose. (See Glue.)

Casein is obtained from separated and strongly diluted milk (cows' milk) by precipitation with acetic acid. The precipitate is filtered, washed with water, dissolved in soda or ammonia, reprecipitated with acetic acid, and this treatment repeated several times. The product is freed from fat by extraction with alcohol or ether and is then dried. Casein is so obtained as a white powder, insoluble in water, but soluble in alkalis, which contains about 15 per cent of nitrogen, and is extensively used both in the food industry (for the preparation of special foods) and industrially, for the manufacture of adhesives, cements, animalization of cotton, and other uses. It has the same ultimate composition as the albumens but contains 0·85 per cent of phosphorus. In milk it is present in solution in a salt-like combination. Solutions of the alkali and calcium salts of casein do not coagulate on heating.

Gluten is obtained as a residue in the manufacture of starch. In the hydrated condition it forms a tough, dough-like, elastic mass of greyish yellow colour, which can be drawn out to threads. After drying it resembles horn. It consists mainly of the gluten proteins, which occur in wheaten flour only, and are otherwise unknown, and which constitute the nitrogenous and highly nutritious constituent of flour. Gluten is insoluble in pure water, but slightly soluble in water containing a little acid or alkali. The proteins of gluten are soluble in alcohol of 60 to 70 per cent concentration. Some of them yield glutaminic acid on hydrolysis. It is believed that gluten contains at least four different proteins: gluten casein, gluten fibrin, gliadin and mucedin.

Glue and Gelatine. There are two varieties of glue, namely skin glue and bone glue. Skin glue is obtained from waste skins. The corium tissue, that is the middle layer of animal skin, which is insoluble in cold water, loses its organized structure in boiling water and dissolves in the form of glue. A quite similar solution is obtained by extraction of bones with boiling water, during which the bone cartilage, or ossein, which is the nitrogenous constituent of bones, also forms glue. Chemically, therefore, bone glue and skin glue are identical. Their essential constituent is glutin, a degradation product of the so-called collagenes. Glutin is an amorphous, odourless and tasteless substance, which swells considerably in cold water without dissolving, but which dissolves in hot water to form a viscous liquid of great adhesive power, which gelatinizes on cooling, even in a 1 per cent solution. Solutions of glutin are precipitated by tannic acid, formaldehyde and alcohol, and by alum and ferric salts in presence of alkali. *Chondrin*, which is contained in cartilage glue, from non-ossified cartilage, is similar to glutin.

Gelatine is the purest glue, free from taste, smell and colour, and obtained from the purest obtainable ossein, by removing the mineral substances associated with ossein by boiling with hydrochloric acid and then dissolving the residual ossein in boiling water. Gelatine differs

from glue (glutin) as it mainly consists of glutose, which has weaker adhesive powers than glue, but has greater gelatinizing powers.

Lichenin, or Iceland moss, is a carbohydrate, being a polysaccharide of the same empirical composition as cellulose, and on hydrolysis with acids it is converted into d-glucose in the same manner as cellulose.

Ossein. (See Glue.)

Pectins are probably oxidation products of vegetable mucins. They are found, for example, in fruit juices and are the constituent which causes these to gelatinize.

Mucilage (Bassorin) is the chief constituent of various varieties of gum, for example of tragacanth and bassora gums, also of cherry and plum-tree gums. This substance swells in water to form a slimy liquid which cannot be filtered. It is readily soluble in alkalis.

Flesh, bone fibre, the entrails of silk-worms, natural silk waste and similar materials have also been either suggested or actually tried experimentally, for artificial silk manufacture. A purely synthetic product has been proposed for the purpose in the form of the polymerization products of halogen vinyl or organic vinyl esters in German patent 281,877 (Austrian patent 70,348). See also German patent 346,832, which deals with lignoprotein.

CHAPTER V

PRELIMINARY TREATMENT OF THE CELLULOSIC RAW MATERIAL

The preliminary treatment of the raw material may serve three purposes. In the first instance, the impurities should be removed so far as possible and, secondly, the material brought into the most suitable form for further treatment. From these standpoints the preliminary treatment is only necessary if the raw material is very impure or is in a form which is unsuitable for further treatment. Thirdly, there are special forms of preliminary treatment, the object of which is to effect a chemical change in the raw material, which will render it more suitable for further treatment.

With regard to purification of the raw material, wood-pulp has already undergone the chemical processes of decomposition of the wood fibre and of bleaching, and is now supplied in such a form and degree of purity by the wood-pulp works that further pre-treatment is superfluous. Occasionally, the wood-pulp is submitted to a short supplementary drying operation, in order to attain as uniform a degree of dryness as possible, which is of importance for the subsequent operations; for it must be remembered that even a consignment which left the wood-pulp works in an absolutely uniform condition with regard to dryness, may have absorbed more or less moisture from the atmosphere during transport, according to the weather conditions, especially in the outer layers of the bales. The supplementary drying is carried out in large drying chambers, heated with steam or hot water, or, better still, traversed by a current of warm air. They are usually so arranged that the sheets of wood-pulp can be loosely stacked in suitable frames, so that the warm air may be able to circulate freely between them. The temperature of the driers is usually not allowed to exceed 40 to 50° C., and drying is discontinued when the material still contains at least 6 to 7 per cent of moisture.

The quantities of wood-pulp which are now treated by many artificial silk works are so large that very large drying plants would be required. Some works, therefore, dispense with the supplementary drying process.

Regarding the form in which wood-pulp is supplied it should be noted that the usual thick sheets of about 400 to 600 gm. weight per sq. metre, can be used directly for viscose manufacture, but that this form is unsuitable for nitration or acetylation, that is, for the manufacture of collodium or acetate silk, as it renders uniform and sufficiently rapid nitration or acetylation impossible. For the manufacture of these silks, the wood-pulp sheets are further treated either in the wood-pulp works or in a paper mill and converted into thin, smooth or crinkled tissue paper, weighing about 10 to 15 gm. per sq. metre.

The various forms of cotton waste, which are more or less contaminated by impurities, require intensive and careful pre-treatment, which is partly mechanical and partly chemical.

The Mechanical Pre-treatment of Cotton. The cotton is transported in a highly compressed state and the object of the mechanical pre-treatment is to loosen it and to remove mechanically admixed and loosely adherent impurities, such as sand, dust, capsules and seed residues and so forth, as completely as possible. The same machinery is used as that employed in the cotton industry for similarly treating spinning cotton.

The first loosening is usually carried out in the opener or in the whipper. In the opener the cotton passes through one or more (for example, four) horizontal drums, the circumferences of which are provided with a number of steel rails carrying projecting teeth. During the rotation of the drums, the teeth engage with similar stationary teeth which are mounted on bars attached to the inner side of the cover of the drum. The cotton is conveyed to the rotating drums by a special mechanism, and is hurled by these on to the stationary teeth and forced between the tooth systems, whereby the compressed bundles of fibres are thoroughly loosened, whilst the adhering foreign bodies, such as sand, foliage, seed capsules,

seeds and so forth, are removed and fall through a grid of thin iron bars lying below the opening drum.

In the whipper, beating arms are attached to two revolving shafts, inside a wooden casing, which are so arranged that whilst these revolve the beating arms of the one shaft pass between those of the other. Further, stationary arms are so fixed within the casing that they coincide exactly with the intervals between the beaters. As will be readily understood, the action of this mechanism is quite similar to that of the opener.

In order to complete the loosening and purifying process, the cotton discharged from the whipper or the opener is usually carried to the scutcher. Occasionally, when the condition of the raw material is suitable, the whole treatment is carried out in the scutcher only. The working part of this contrivance is the so-called beater, which consists of two or three steel bars, which are attached by means of several triangular fork frames to a shaft which rotates within a casing at the rate of 1,500 to 1,800 revolutions per minute. The cotton which is fed into the machine is caught up by the rotating beaters and hurled on to the triangular bars of a grid placed below the beater.

Any remaining tangled masses of fibre are thus loosened and all the coarser impurities fall through the grid, whilst the fibres pass into the so-called fly chamber, where they are assembled on to a cylindrical sieve, with the help of a partial vacuum, in the form of a thin fleece, which is detached from the other side of the drum.

There are also scutchers in which the beater is replaced by a so-called carding arm. In these machines, instead of sharp-cornered bars, the beater carries wooden laths, provided with a large number of sharply-pointed teeth, which beat, tear and comb the fibres. It is said that this machine loosens and purifies the cotton more effectively than the beater scutcher and also does less damage to the fibre.

The last machine to be considered here is the breaking machine. This machine is never used until the cotton from the machines already mentioned has undergone chemical treatment, that is, degreasing and bleaching. The fibres, which have been

thoroughly wetted in the course of the chemical treatment, adhere partially on drying and are, therefore, treated in the breaking machine in order once more to loosen them. This is effected by further beating by means of the rapidly rotating drums of the breaker, which usually contains two or three of these.

The mechanical pre-treatment is of special importance in the case of linters (see page 30) whilst spinners' waste is usually free from mechanically admixed plant residues and therefore requires less drastic mechanical pre-treatment.

Chemical Pre-treatment. This is, of course, also governed entirely by the condition of the material. Linters contain comparatively small quantities of fat, namely just their own natural grease, but are on the other hand usually heavily contaminated with admixed vegetable fragments. These latter hardly occur in spinners' waste, which, however, usually contains a very much larger amount of fatty matter, namely, not only their natural grease, but that introduced during spinning in addition.

Consequently, a simple degreasing process usually suffices in the case of spinners' waste, and consists in boiling for several hours with dilute soda solution, of about 2 per cent concentration, to which a little caustic alkali may be added. Even in the case of linters a 2 to 4 hour boil in an open pan with a mixture of soda and caustic soda often suffices (2 to 5 per cent NaOH and 2 to 3 per cent Na_2CO_3) by which means the fat is dissolved, and any vegetable impurities which may have escaped the mechanical pre-treatment are removed or so far attacked that they disappear during the succeeding bleaching operation. This treatment does not, however, always suffice. Sometimes a more intensive chemical treatment is required, which consists in boiling for many hours with caustic soda, alone or with soda, under pressure. For this purpose the cellulosic material is treated with from 10 to 20 times its weight of a solution containing 2 to 3 per cent or even more caustic soda together with about the same weight of sodium carbonate.

For this operation, apparatus is often used in which the lye is forced through the material with the aid of a pump, for example, the sectional digesters of the firm of Fr. Gebauer,

of Charlottenburg. The lye, at a temperature of 120° C. and of the above composition, is forced through the material at an excess pressure of about 1 atmosphere. The process is complete in from 2 to 4 hours. The lye is then withdrawn and replaced by water, which is also pumped through the material in the same manner and renewed as often as may be necessary until the alkali is completely removed.

Boiling can, of course, also be carried out in ordinary digesters, without circulating the liquor with pumps. Also, for the subsequent washing the ordinary washing vat or similar plant may be used, for example, the rinsing machine of Fr. Gebauer.

Special methods of treatment are required when the material has to be chemically modified, in order to render it more suitable for the following solution or other processes. Such processes are readily understandable if one bears in mind the fact, already discussed in the section on Cellulose (page 27), that, as supplied by Nature, it undoubtedly represents a large molecular aggregate, a multiple of $C_6H_{10}O_5$, and that this aggregate is unable to go into solution as such, but only after a sufficient degree of depolymerization. This depolymerization is achieved by different methods in the various processes, and will, therefore, be more closely discussed in the special section. It can be effected by either acids or alkalis. In the case of collodium silk, for example, it is effected by warming the cellulose to temperatures of 120 to 180° C. before nitration, or by the action of the acids during nitration. It is effected in a similar manner, during acetylation, in the acetate silk process, when cotton itself is used and not hydrocellulose, which has already undergone degradation. In the viscose and cellulose ether silk processes, the pre-treatment with alkali effects the necessary depolymerization. In the case of cuprammonium silk it occurs simultaneously with the solution process, under the influence of the ammonia, perhaps under the oxidizing effect of the copper oxide. As, however, ammonia is a much weaker alkali than potassium or sodium hydroxide solutions, the depolymerization of the cellulose molecule and consequent solution is comparatively slow in this case. It can be assisted to an extraordinary extent, as has been shown by Fremery, Urban,

and Bronnert, by suitable alkaline and oxidizing pre-treatment, as will be described in the special section.

In German patent 217,316, O. Glum & Co. propose to heat the cellulosic raw material to temperatures above 100° C. in a liquid which is stable at such temperatures, such as glycerine, oil and so forth, whereby it is alleged that the cellulose, or the compound obtained therefrom, becomes more soluble.

In German patent 290,131, the Verein für chem. Industrie, Frankfurt-am-Main, proposes to render cellulose more soluble by treating and drying it with such small quantities of acids or acid salts that no formation of oxy- or hydrocellulose occurs.

According to Roederer's German patent 338,551, the raw material is treated with formaldehyde or its derivatives, in presence of acids, bases or salts, in order to render the silk more resistant to water, atmospheric influence, light, and so forth. This action is essentially improbable, as the reaction alleged in the patent to take place between cellulose and formaldehyde does not, in effect, occur. The worthlessness of the patent was soon confirmed by the circumstance that it was allowed to lapse.

The bleaching of the cellulosic raw material, which usually follows, is carried out as usual, preferably in a bleaching kier with weak bleaching powder solution or electrolytic bleach. According to the character of the raw material and of the preceding alkaline treatment about 2 to 6 per cent of chlorine is used, corresponding to about 6 to 18 per cent of bleaching powder, calculated on the dry raw material. Bleaching is usually followed by the usual scouring, repeated, and thorough washing (for example, centrifugal washing) and drying.

Cotton, cotton waste, and so forth are dried in capacious drying chambers, preferably by hot air which passes over the material which is spread on frames. As the fibre usually coheres more or less during drying, it must, as already mentioned, be loosened once more after drying, in suitable machines, such as the opener (see page 62). It is then ready for solution, esterification, or other similar process.

The bleaching and drying of wood-pulp has been dealt with specially on pages 52 to 54.

Some works handle cotton waste in the form of sheets, by treating the raw material in the same manner as wood-pulp, namely by washing in kiers, dehydrating on the Foudrinier machine, and drying on drying cylinders.

CHAPTER VI

THE SPINNING SOLUTION

Cellulose Solutions. The next problem in the production of artificial silk is the conversion of the carefully prepared raw material into a solution suitable for spinning. The problem was by no means easy, as but few solvents for cellulose were available. There were two possibilities. One could either dissolve cellulose itself in a specific solvent, such as ammoniacal copper oxide or zinc chloride, or one could convert it into certain derivatives for which suitable solvents were known. Both methods were successfully followed in practice, but the latter method first, as it so happened that the first solvent for cellulose itself, ammoniacal copper oxide, was only discovered twelve years after the discovery of cellulose nitrate.

As one can only properly describe as a " solvent " of a substance a liquid which dissolves it without changing it chemically, there are actually no true cellulose solvents. For, as already mentioned, the few compounds which we are in the habit of describing as cellulose solvents do not leave cellulose unchanged. However, the changes produced by these in the cellulose molecule are so slight, provided that their action does not extend over an excessively long period, that in practice one may speak of solutions and solvents in this case. Other conditions are met with in the case of cellulose esters and ethers, that is of cellulose nitrates, and acetates, ethyl celluloses, and so forth, which dissolve without change in organic solvents to form very stable solutions.

It must, however, always be borne in mind that even these are not true solutions, but colloidal solutions, or, more exactly, dispersions of the cellulose or cellulose compound. According to R. O. Herzog, expressed in the language of colloidal chemistry, the smallest cellulose particles, or crystallites, are converted into micellae, which are the small particles in colloid solution. During the spinning process, the converse action

takes place, namely, transformation of the micellae into crystallites. (See page 27.)

Properties of Spinning Solutions. Not every solution of cellulose or of a cellulose derivative is suitable for the production of artificial silk. This is only the case if the solution fulfils certain conditions.

Firstly, the formation of a continuous thread is only possible if the solution possesses a certain viscosity. For example, if a rod is dipped into the solution and then removed, the solution should not remain attached to the rod in the form of a compact mass, like soft soap or a material of similar consistence, nor should it detach itself in drops, like water for example, but must flow off in a uniform, threadlike stream, like an oil. This viscosity is due to the internal friction of the molecules or molecular complexes, flowing one over the other.

Every liquid or gas shows a certain internal friction or viscosity. If the viscosity of water is taken as unity, then that of air is 0·018, of olive oil ·87, and of pure glycerine about ·300. Thus the magnitude of the viscosity is of importance. The above-mentioned comparisons show that the viscosity of soft soap is too high and that of water too low for the production of a uniform thread.

The viscosity depends on various factors. Firstly, it is dependent on the temperature, and falls as the temperature is raised, under otherwise unchanged conditions. In the case of solutions it is also dependent on the concentration and on the molecular condition of the dissolved substance. These two factors are of especial importance in our case, for it follows that solutions of cellulose or its derivatives for spinning purposes must have a definite concentration and that the degree of molecular dissociation or depolymerization of the dissolved substance is by no means indifferent. In actual practice, cellulose solutions which are too dilute are as unsuitable for the production of a filament as are those in which the cellulose molecule has been too far dissociated by hydrolysis, acetolysis, or depolymerization, for example, in consequence of the excessive action of alkali. Too high a viscosity, on the other hand, not only leads to faulty formation of the fibre, but makes it difficult

or impossible for the solution to be filtered and forced through the extremely fine apertures of the spinning nozzles. Even when this is still possible, too viscous a solution can only be spun into thread at a relatively slow speed, which causes the output to be small.

The concentration of the solution also affects the strength of the filament, as when produced from more concentrated solutions, the fibre, within certain limits, is produced of greater density, and is, therefore, stronger, whilst dilution impedes the tendency of the molecules to adhere closely during coagulation.

Apart from the low viscosity of the solutions, which could sometimes be corrected by increase in the concentration, the uselessness of solutions the cellulose in which is greatly degraded is due to another cause. The capacity to form a thread is not sufficient for the success of the spinning process. The fibre must also be sufficiently strong, and this is not the case if the solution contains a strongly degraded or depolymerized product. One of the main objects of the pre-treatment of the cellulosic raw material is, therefore, the production of the most favourable size of particle.

Finally, if the spinning solution is to yield satisfactory results, the fibre-forming substance must be capable of precipitation in a suitable condition. The thread must, of course, consist of the separated cellulose or cellulose derivative. The solution must, therefore, permit an easy and more or less complete separation of dissolved substance from the solvent on precipitation, without any interference with the shape of the thread. This separation may take the form either of simple evaporation of the solvent (dry spinning), or of precipitation of the thread in a suitable precipitation bath (wet spinning). In the latter case in particular, all by-reactions which might disturb the production of the thread through gas evolution or other decompositions must be avoided.

It is also of the highest importance for manufacture that the spinning solutions should always be produced of the greatest possible uniformity. Any change in the spinning solution entails corresponding changes in the further treatment, and, above all, in the spinning process, which are bound to

give rise to continuous difficulties in such a complicated process, in which everything has to interlock like the wheel-train of a clock. Finally, it is obvious that the purity of the solution is an extremely important factor. As the solution is required to pass uniformly through the very fine openings of the spinning nozzles without interruption of its continuity, it must be entirely free from all insoluble particles of all kinds and also from bubbles of air or other gases. The former would obstruct the tubes and the latter would interrupt the stream of liquid at the end of the nozzle ; thus either would cause rupture of the thread.

Some spinning solutions are very unstable. Solutions of this kind alter more or less quickly after preparation and pass through certain intermediate stages before complete decomposition. Such solutions are frequently not capable of being used for spinning under ordinary conditions immediately after being prepared, but only at a later stage. It is only when this stage is reached that they are " ripe " for spinning. This condition of ripeness must, therefore, be waited for before the solution is spun. The passage through the various stages until the solution is ripe for spinning is known as the ripening process. This is greatly accelerated by warming. It is of great importance, particularly in the preparation of viscose silk, and will, therefore, be discussed at length in connection with that process.

Preparation of the Spinning Solution. From the foregoing it will be clear that the main object in the preparation of a spinning solution must be to obtain concentrated solutions with a sufficiently high, but not too high, viscosity from a cellulosic material which has been but slightly degraded. It has already been explained that a certain degree of depolymerization of the cellulose molecule is desirable or necessary. It has also been explained how such a depolymerization is achieved, and we will return to this question when discussing the special methods of preparation. Cellulose can only be dissolved with dissociation of its complex molecule, and this degradation of the molecular complex is associated with increased solubility but decreased fibre strength. It is one of

the most important, and often most difficult problems, in preparing a spinning solution, mutually to adjust the viscosity and concentration. The methods by which this adjustment is achieved vary with the character of the solution, that is, more especially with the character of the particular kind of artificial

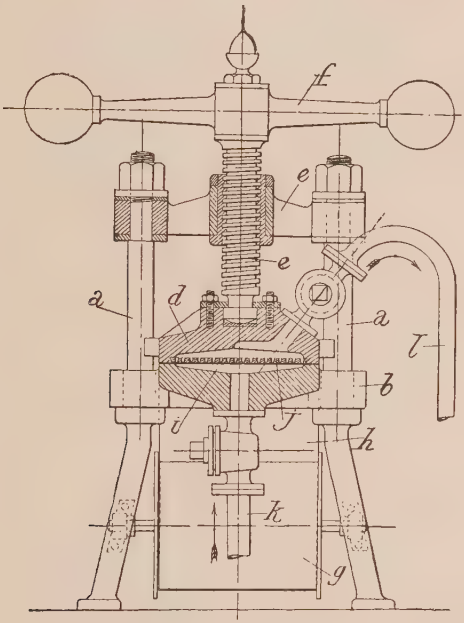
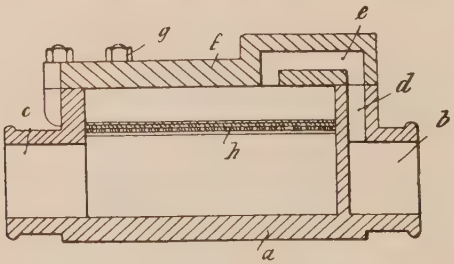
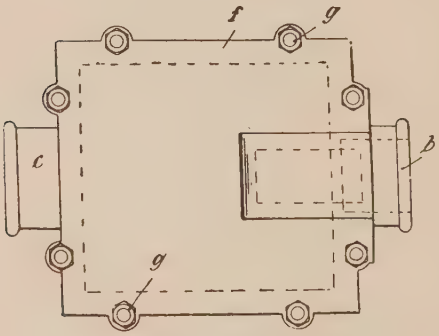


Fig. 8. Lumière Filter-press

silk process, and will be discussed for each particular process. We need only note here, that the viscosity of the spinning solutions can usually be adjusted within wide limits by suitable pre-treatment of the raw material, by which means an optimum particle size can be achieved. The uniformity of the spinning solution, already referred to, naturally demands the closest observance of the prescribed method of working, but always with the reservation that modifications must be made to allow for any irregularities in the raw material. For, as mentioned, the operator must understand how to compensate for any unavoidable irregularities in the raw material by suitable means.

So far, the cuprammonium silk process is the only one in which the cellulose is dissolved as such. Salt solutions, such as zinc chloride, calcium sulphocyanide, calcium bromide solutions and others have only been tried as solvents experimentally. In all other artificial silk processes, solution is





(*Rheinische Kunstseidenfabrik A.-G.*)

FIGS. 9A AND 9B. FILTER

preceded by certain reactions, the cellulose derivatives being then dissolved. Such reactions are nitration for collodium silk, acetylation for acetate silk, formation of xanthate for viscose silk, and so forth, as described in the Special Section. The plant required for the production of the spinning solution varies according to the chemical process used, but in general the pans with stirrers or kneading devices commonly used in the chemical industry are employed.

According to German patent 384,404, E. Schülke first converts the material to be converted into a spinning solution, such as cellulose xanthate, into a dough, which he then divides into bands or threads and

forces into the solvent in the dissolving tank, in order to accelerate the dissolving process, reduce the power consumption, and prevent foreign bodies from being introduced into the liquid.

The purification of the spinning solution, that is, the removal of all insoluble particles, is achieved by careful filtration. For this purpose, ordinary chamber filter-presses are generally used, with the usual filtering media, namely woollen or cotton cloths, cotton wool, and so forth. In the case of cuprammonium-cellulose solutions only, these latter materials are inapplicable, as they are destroyed by such solutions. Sand filters were formerly used in this case, which were later replaced by very fine iron or nickel gauze. Asbestos cloth is also sometimes used. As it is absolutely necessary that even the smallest insoluble particles should be removed, multiple filtration is usually employed. But, even so, impurities may get into the solution from the piping on its passage to the spinning machine or to the nozzles, and, therefore, not only is a further filter-press usually interposed immediately in front of the spinning machine, but the liquid is caused to pass through one or more filters on the machine itself, a matter which will be further dealt with when describing such machines.

A peculiar type of filter-press is described in German patent 170,935, of Lumière Brothers, and is depicted in Fig. 8. The novelty in this filter consists in a continuous band of filtering fabric *i*, which can be advanced step by step and clamped between the two parts *b* and *d*, which together form the filter-chamber, so that the filtering surface may be very rapidly changed. When the portion of filter-cloth in immediate use is choked, the inlet and outlet pipes *k* and *l*, for the spinning solution are closed, and the pressure head *d* is lifted. On turning the screw head *f* downwards, the filter-cloth *i* is advanced and reclamped under the sieve *j*, after which the cocks are re-opened and filtration proceeds.

The renewal of the filtering surface is not quite so convenient in the filter described by the Rheinische Kunstseidenfabrik A.-G. Aachen in German patent 246,780, and depicted in Figs. 9A and 9B. It consists of a filter chamber *a*, covered by a lid *f*, which contains the filter *h*. The spinning solution to be filtered enters the chamber at *b*, rises through the channels *d* and *e* and on to the filter, after passing which it is discharged through the opening *c*. The apparatus is said to ensure a particularly good distribution of the spinning solution over the filter. It is also stated that the filter can be changed easily and without loss of liquid, as in order to expose the filter-plate it is merely necessary to remove the screws *g*, and lift the lid *f*.

German patent 245,440, by Soie de Basècles, describes a filtering arrangement rather like a filter-press, constructed of lens-shaped units with radial ribs and cavities.

The pressure filters used in some works offer the advantage that filtration is possible under considerable pressure. Consequently a thicker filtering layer can be used and a clearer solution thus obtained.

See page 246 with regard to the cleansing of filter-sieves, more particularly for cuprammonium solutions.

Air and gas bubbles are removed by careful de-aeration of the filtered solutions. By mere standing for a long period the

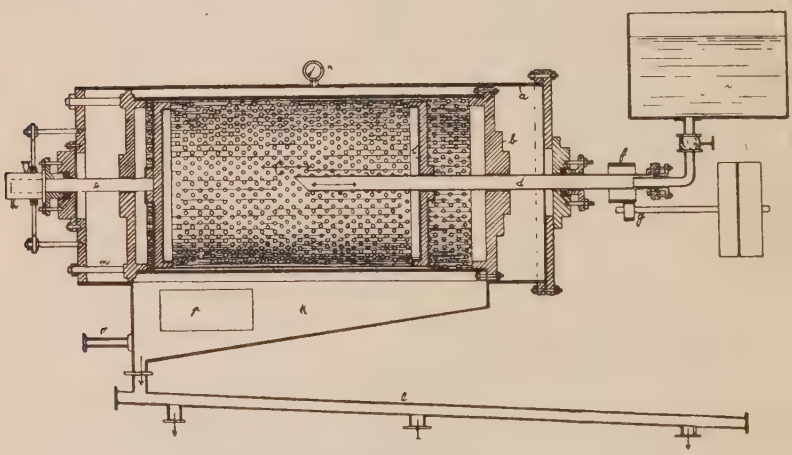


Fig. 10. Thilmany De-aerator

bubbles rise to the surface if the solution is sufficiently mobile. This latter method is the only one possible if the spinning solution has been prepared with a volatile solvent (for example ether-alcohol in the case of collodium silk), in which case evacuation and warming are not permissible. In other cases, however, de-aeration can be accelerated by the application of vacuum, assisted on occasion by warming. The de-aeration process may proceed simultaneously with the ripening process already referred to, as both require that the spinning solution shall stand for some considerable time.

A special contrivance for de-aerating viscous solutions and similar materials, and more especially spinning-solutions for artificial silk, which can be interposed in closed circuits, is described in A. Thilmany's

German patent 317,869. Fig. 10, shows a longitudinal section of the apparatus. In order to operate it the contrivance is well evacuated, the cock of the storage tank *i* is opened and the inner drum set in motion. The mass flows through the tube *d* into the cylindrical sieve, is aspirated through the perforations in the sieve, ground and kneaded between the two cylinders, and then drawn through the perforations of the outer cylinder. It is stated that by these means even the finest air suspension is removed, and that an air-free liquid is discharged through *k* and *l*.

A special vacuum de-aerating apparatus is described by B. Borzykowski in German patent 411,313.

When the spinning solution, of correct composition, has been sufficiently purified by filtration, completely freed from air-bubbles by de-aeration, and finally ripened, it may be conveyed to the spinning machine.

CHAPTER VII

THE PROCESS OF SPINNING ARTIFICIAL SILK

The Spinning Process Proper. In the course of many years practically no change has taken place in the general principles of the spinning process for the manufacture of artificial silk. This product is still spun according to precisely the same principles as were described by Ozanam in 1862, and which was operated on a large manufacturing scale by Chardonnet forty years ago, in 1885 (see pages 4–6). This principle corresponds in many ways to the process used by the silk-worm to produce natural silk, which we described in our preface. The artificial silk fibre is produced by forcing the spinning solution, which contains the fibre-forming substance in solution, under pressure through very fine openings, after which it is coagulated. The coagulated fibre is simultaneously drawn out to a fine thread, which then solidifies completely, or is fixed by special means. By the assemblage of a considerable number of individual threads a main thread is formed, which is wound on to a revolving spool or other contrivance. The winding gear also withdraws and stretches the fibre.

Coagulation can be effected in various ways. If the spinning solution has been produced with low boiling solvents such as methyl or ethyl alcohol, ether, acetone, and so forth, which readily evaporate in the air, the solution coagulates when the liquid is exposed to the atmosphere, by evaporation of the solvent, and such solutions can, therefore, be simply spun in air alone, which may be warmed, without any other coagulant. This method is known as the dry spinning process. As certain cellulose derivatives only, more especially esters such as cellulose nitrate, cellulose acetate, and so forth, are soluble in organic solvents of low boiling point, but not cellulose itself, the dry spinning process can only be used in the preparation of collodium and acetate silk, and may later be used for cellulose ether silk.

Attempts have also been made to spin cuprammonium silk in the air, by the dry method, with and without a spray of a precipitating medium. (See pp. 253, 254.)

The silk fibres obtained by the dry spinning process naturally consist of the dissolved compounds themselves, for example of unchanged cellulose esters or ethers. In these cases the spinning process is of a purely physical character, without any chemical change. The threads consist of the chemically unchanged evaporation residue of the spinning solution. The conditions differ in the case of the aqueous solutions of cuprammonium cellulose or cellulose xanthate. Such a solution does not usually evaporate sufficiently quickly to form a thread on exposure to the air. Moreover, the cellulose compounds present in these solutions, cuprammonium cellulose and cellulose xanthate, have to be chemically decomposed, and the resultant thread consists of cellulose or cellulose hydrate. This decomposition can, however, be carried out after the formation of the thread in some cases, in which, for example, the thread consists in the first instance of coagulated cellulose xanthate. These aqueous spinning solutions are, therefore, usually spun with the help of a coagulating medium, which may also serve simultaneously as a decomposing agent, the spinning or precipitating bath, into which the spinning solution is squirted from fine nozzles. This procedure is known as the wet spinning process. Solutions of cellulose nitrate and acetate, which can be spun by the dry process, may also be spun in suitable precipitating baths, that is, by the wet process. (Further particulars regarding spinning baths will be found in the next section.)

An interesting theory on the formation of the filament was given by Otto N. Witt (*Die künstlichen Seiden*, L. Simion Nachf., Berlin, 1909, pages 6 and 7). He assumes that the stream of liquid emitted from the nozzle first becomes coated with a pellicle of coagulated material, which is ruptured as the fibre is further stretched and is so divided into a series of individual rings, between which the internal, uncoagulated liquid is exposed, and is in turn covered with a coagulated pellicle through the action of the bath, and so on until the

whole structure has attained the desired degree of fineness and is fully coagulated. Witt compares the whole process to the extension of a telescopic tube. There is no doubt that this explanation is a near approximation to the truth, but it can scarcely be assumed that the pull on the fibre, which is in one direction only, ruptures the thread with formation of separate rings. It may more probably be assumed that the outer, coagulated, tube-like pellicle in the vicinity of the nozzle, slides over the inner core which is still perfectly soft. If, therefore, one imagines the eyepiece of the telescope to be held firmly, close to the outlet of the spinning nozzle and the objective to be pulled out, this would correspond to the process of artificial silk spinning, excepting the fact that in the latter case further material is constantly supplied through the nozzle and the thread does not, therefore, taper in the same manner as the extended telescope. According to Ost, the extension in length of the fibre already occurs within the nozzle.

The stretching of the fibre is often carried very far, and fibres of extraordinary tenuity can be produced in this manner. The process of spinning whilst stretching was very completely developed in the case of collodium silk, and especially of cuprammonium silk, and latterly in the case of viscose silk also. For this modification of the spinning process the nozzle openings may be comparatively wide, namely, 0·25 to 0·5 mm. (For further details see page 138 and also the Special Section.)

Apart from the nature of the spinning solution and the composition and temperature of the spinning bath (see below), other variable factors are of great importance in carrying out the spinning process and must, therefore, be considered. These are, diameter of nozzle aperture, rate of withdrawal, and effective length of bath, that is the length of the track pursued by the filament in the spinning bath. Within certain limits these factors show a certain dependence on one another. The relationships have been studied most closely in the case of viscose silk and further details will be found in the section dealing specially with that material. In general we can only say that these factors vary greatly, not only with the kind of artificial silk which is manufactured, but also, in the case of

any one kind of silk, with the particular manufacturing conditions. For example, the length of passage through the bath may be from 10 cm. to 1 metre and over. The rate of withdrawal of the thread, which is usually about 40 metres per minute in the case of ordinary spool machines, may be increased, for example, to double that amount in pot-spinning machines.

The description of spinning apparatus in the next chapter will afford an opportunity of acquiring more detailed knowledge of the spinning process in all its details.

Simultaneous Spinning and Twisting. The spinning process supplies a bundle of filaments (main thread) which consists of a number of individual, parallel filaments. In order to obtain a thread which can be used for weaving or for other purposes, these must be twisted as in the case of all textile fibres. As we will learn in the section on finishing artificial silk (pages 147 *et seq.*) this is usually carried out on the ordinary multiple twisting or doubling machine. It was, however, fairly obvious that twisting might be carried out, at least in part, together with the spinning process. This procedure offered the further advantage that a thread would be obtained which would better resist the stresses incident to the further manufacturing process, as it is well known that twisted threads are almost always stronger than untwisted threads.

There were, more particularly, two methods by which this result could be achieved, namely, either to revolve the nozzle rapidly, and so obtain a twisted thread in the spinning bath itself, or so to arrange the winding machinery that the untwisted thread should acquire a twist during the winding process. One could also twist the thread between the nozzle and the winding contrivance, for example, by a rotary motion of the precipitating bath or by rolling it on rotary rolls. All these methods were attempted, but the use of rotary spinning-pots (spinning-centrifuges, see pages 131 *et seq.*), for winding was alone a complete technical success. In the case of rotary nozzles (see pages 108 *et seq.*), the difficulties and disadvantages were found to be too great, so that they found no extended technical application, whilst eddying baths and rolling of the thread were found to be even more unsuitable.

SPINNING BATHS

Not all precipitants of cellulose solutions can be used, without qualification, in spinning baths. A bath which precipitates the solution of cellulose or cellulose compound, in the form of an incoherent loose mass, by more or less rapid decomposition, which may be accompanied by much gas evolution and separation of other products, is obviously unsuitable for the purpose. By-products which may be present in the spinning bath may also lead to similar decompositions and other disturbances. A spinning bath is only suitable for the production of a filament if it precipitates the filament-forming material, usually cellulose or one of its compounds, as a homogeneous coagulum, which is at first plastic and which can readily be stretched to a thin thread, without interruption of the continuity of the mass by by-reactions, gas evolution or similar disturbances.

The bath must, therefore, be both a coagulating agent for the filament-forming substance and a solvent for the liquid or liquids in which this is originally dissolved. The composition of the spinning bath must, therefore, depend on the character of the spinning solution, and both on the nature of the cellulose product and of its solvent. The spinning baths will, therefore, be discussed in the course of the special descriptions of each process.

The active constituents of spinning baths may be alkalis, acids, or neutral compounds such as salts, organic liquids, water, and so forth. The coagulating effect of a spinning bath and the consequent speed at which coagulation occurs, usually increases with the temperature at which it is carried out, and also, in the case of solutions, for example of salts and acids, with increasing concentration of these. These two factors must, therefore, be strictly controlled.

A precipitating bath may either have the single function of coagulating the filament-forming substance or it may also be required to take part in a chemical reaction. The latter is the case if the filament-forming compound is present in the spinning bath in the form of compound which must be decomposed to form the filament, because one component only, usually

cellulose, is capable of forming a durable thread. This is the case, for example, with viscose and cuprammonium silks. Even in such cases, it is usually possible first to coagulate in a preliminary spinning bath, without decomposing the compound, and then to carry out the decomposition by subsequent treatment, known as fixation, in a second bath. This method is more particularly applicable to the so-called stretch-spinning processes, as it is much easier to stretch a filament which is only coagulated and is still very extensible, than one which has been more or less completely fixed.

In the choice of materials for the spinning bath the question of cost is, of course, important. Among baths which are otherwise equally effective, those which can readily be regenerated are of course preferred. Such regeneration is easiest in the case of baths which merely remove the solvent in the spinning solution, without the occurrence of chemical reactions of any kind. But where, for example, an alkaline spinning solution is precipitated by acids, a gradual neutralization of the spinning bath obviously occurs and, consequently, a continued supply of chemicals is necessary for regeneration. In such a bath, the acidity must naturally diminish steadily during the spinning process. In such cases it is, therefore, particularly necessary to employ a flowing bath which circulates continuously through the spinning tank, in contrast to the standing bath which is used until it has absorbed a certain proportion of material from the spinning solution, which is, however, an unsatisfactory method, as it tends to disturb the uniformity which should exist between all portions of the filament.

Additions to the Spinning Bath. Apart from the actual precipitants, other substances are frequently added to the spinning bath with the object of favourably influencing the formation of the thread, by making it more flexible, more brilliant, and so forth. For example, additions of glucose, molasses, glycerine, lactic acid, ethylene thiohydrin, and other substances are recommended. Such additions must, of course, be chosen with due regard to the character of silk, spinning solution, and spinning bath, and will, therefore, be further considered in the special section. The same considerations apply to those

additions to the spinning bath which are made for special reasons, such as the addition of heavy metal salts to viscose baths, in order to precipitate sulphides on to the filaments and so prevent adhesion of the filaments, and other similar additions.

Hanging Liquid Columns as Spinning Baths. Several attempts have been made to arrange the spinning bath in the form of a hanging column of liquid, carried by the outer, atmospheric pressure. The intention was that the diminished pressure, which could be varied at will by altering the height of the column and the rate of flow of the liquid of which it consisted, should assist the discharge of the spinning solution from the nozzles. With regard to the apparatus for this purpose, we must refer the reader to page 112, on which the patents dealing with this subject are referred to. These processes have not proved commercially successful.

Baths with Several Layers of Liquid. It was occasionally anticipated that an advantage would be gained by passing the fibre through the first coagulation bath directly into a second bath which possessed a different power of coagulation. Such double baths were, for example, proposed by Crombie and Schubert, and also by Ping and Schubert (see page 112) in a suspended column. Such baths have not been technically adopted as it is simpler to use two consecutive adjoining baths. Further details on the proposed apparatus will be found on page 129. (See also Fig. 52.)

Electric Precipitation. In British patent 6385/1900, U.S. patent 745,276, and Austrian patent 14,566, J. F. Cooley proposes to introduce the spinning solution in a finely divided condition into the field of a convective electric discharge, whereby it is alleged that the solvent is volatilized and the dissolved substance separated in the form of more or less fine filaments. A. Thilmany arranges the spinning nozzles in the bath between two electrodes which are also immersed. Apparently, precipitation is supposed to occur under the influence of the ionic migration. It is stated that the precipitated filament is hardened and freed from adherent salts by the further action of the current, whilst the decomposed salts migrate to the cathode. Processes of this character are too complicated and expensive.

CHAPTER VIII

THE SPINNING MACHINE

The spinning machine forms the focus of the whole process of producing artificial silk. In more senses than one, all the threads of the process converge at this point, which forms the cradle of the fibre, in which it is endowed with faults and virtues which follow it throughout life, and where its value or worthlessness is first decided.

The essential parts of any spinning machine are: the iron framework, on which all the other parts are arranged; the spinning bath containers; the feed-pipes for the spinning solution, which are usually provided with spinning pumps and filters; the spinning nozzles which terminate these; the inlet and outlet pipes to the spinning bath, and, finally, the winding gear, including guides for the thread, and so forth. Dry spinning machines, which may be used for collodium or acetate silk, are not, of course, provided with spinning vats nor with the corresponding piping.

Spinning machines can be classified in various ways. Firstly, they may be classified according to the method of winding the thread, from which standpoint those machines which are mainly used may be divided into bobbin machines, reeling machines, and pot spinning machines. According to the nozzles with which they are provided, machines may be divided into those with multiple nozzles and with single nozzles. Finally, spinning machines may be classified according to the type of thread produced, into those producing normal artificial silk, artificial horsehair, staple fibre, and so forth.

Fig. 11 shows a section of a bobbin spinning machine as supplied by Oscar Kohorn & Co., of Chemnitz and Vienna, and Fig. 12 a pot spinning machine from C. G. Haubold, Chemnitz. (Fig. 55, facing page 132, shows a pot spinning machine by Oscar Kohorn & Co.) The arrangement of a reel spinning frame may be seen in Fig. 52 (page 130), which shows a construction

according to German patent 168,171 of Société Française de la Viscose.

Dry spinning machines are specially characterized by the fact that the thread and winding bobbins are situated in a closed casing, so that the evaporated solvent or other vapours or gases may not escape into the outer air, but may be led away

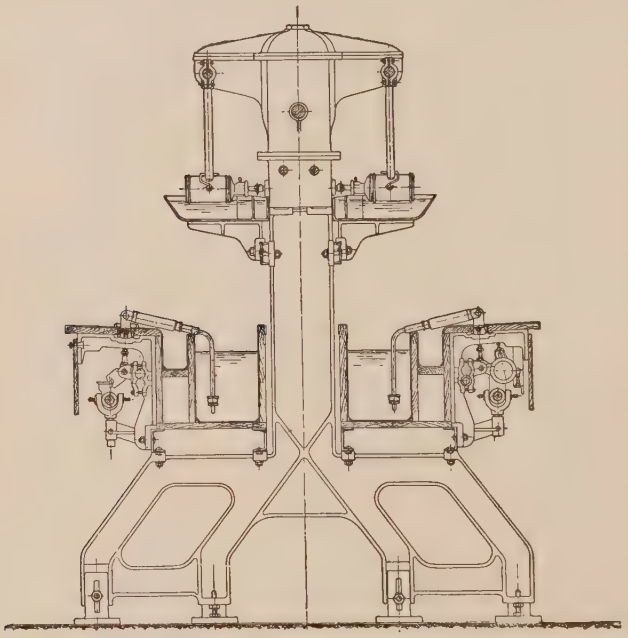


Fig. 11. Bobbin Spinning Machine of Kohorn & Co., Chemnitz

through a collecting main. Either the whole machine is enclosed, so that all the nozzles are within a common casing, or each thread is enclosed in its own special casing, by means of which it is isolated from the surrounding atmosphere. Occasionally, several nozzles are grouped together in one casing. The course of the thread, winding operation, and so forth are observed through sight-glasses.

A machine for dry spinning in vacuo is described by M. Denis in German patent 277,154. The device is too complicated and expensive to be used commercially.

In order to maintain the uniform temperature in the spinning chambers which is necessary in order to produce a uniform thread in dry spinning, the Rhodiaséta Company of Paris has designed a temperature regulator which is described in German patent 410,723.

We will now consider the spinning machine in detail, in the order in which it is traversed by the thread.

The filtered and de-aerated spinning solution is conveyed

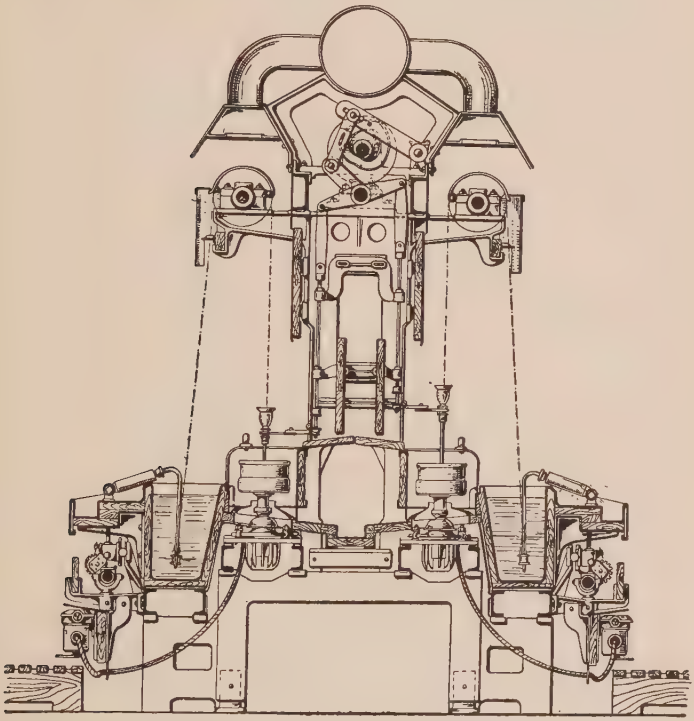


FIG. 12. POT SPINNING MACHINE OF C. G. HAUBOLD, CHEMNITZ

from the storage tanks to the spinning machine either by air pressure, or, for example, in the case of thick collodium solutions, by hydraulic presses, or, finally, by pumps which withdraw the solution and force it forward. Initially, when the pressure of these pumps was used directly for forcing the solution through the spinning nozzles, it was soon found that the filament was of very uneven thickness. Individual nozzles,

which were partially blocked, allowed less spinning solution to pass and the increased pressure so produced forced a still larger quantity of solution through the remaining unblocked nozzles, causing thicker threads to be formed in these. Moreover, where a considerable number of jets are present the pressure at the far jets is less than at the nearer jets, owing to frictional resistance in the piping, and this also causes inequalities in the thread.

Now, uniformity in the thickness of the thread is one of the most important qualities in any textile fibre, and is, therefore, an absolutely essential requirement for artificial silk. In spinning artificial silk, the following factors control the thickness of the thread—

1. The proportion of fibre-forming material in the spinning solution.

2. The quantity of spinning solution forced through the nozzle in unit time.

3. The rate of withdrawal, which is dependent on the winding speed, and

4. In the stretch-spinning process the degree of stretch of the fibre, which is dependent on special adjustments.

It is not difficult to ensure uniform concentration of the spinning solution. As already mentioned, it is only necessary to adjust the viscosity and concentration by suitable pretreatment of the raw material. The rate of withdrawal and degree of stretching of the fibre are dependent on the mechanical adjustment of the component parts of the machine which can be effected without difficulty. The greatest difficulties are associated with the attainment of a constant flow of spinning solution per unit of time through the nozzles, which requires particularly careful attention for the reasons already mentioned.

Regulators for Supply of Spinning Solution. Various methods have from time to time been tried for regulating the rate of supply of spinning solution to the nozzle.

The first device proposed for this purpose, more especially for spinning viscose silk, was the regulator described by Chas. F. Topham in British patent 10,029/1901, German patent 138,507, and Austrian patent 12,388, which is shown in Fig. 13. The cylinder *C* contains a float *B*, to which the conical valves 2 and 3 are rigidly attached. The

spinning solution enters the cylinder *C*, through the tube *e*, and the valve apertures 4 and 5 and passes on through the tube *d*, to the nozzle *D*. The float *B* is adjusted by weighting with mercury or the like in such a manner that with increasing pressure it rises into the guiding channel 11 in the stopper 10, and throttles the valve openings 4 and 5 by means of the conical valves 2 and 3, opening them again as the pressure drops. The intention was that in this manner a uniform flow of liquid should be attained independently of the pressure. In order to prevent the float from seizing it was provided with a spiral channel so that it was constantly revolved by the flow of liquid. The contrivance did not operate in practice according to theoretical anticipations, and was therefore not commercially successful.

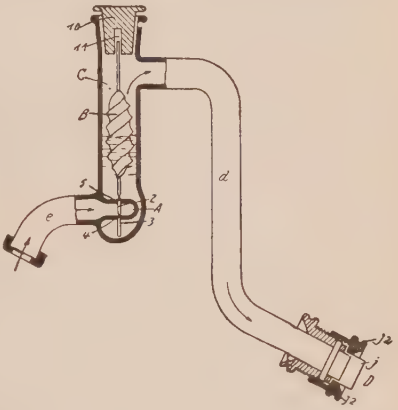


Fig. 13
Topham Flow Regulator

Many attempts were made to solve the problem by the use of very accurately adjustable cocks in the spinning solution supply pipe, such as were patented, for example by Soc. de la Viscose (German patent 163,467 and French patent 345,293) and by L. Morane (British patent 24,707/1910 and French patent 410,267). These cocks were also unsuccessful in practice. Apart from the fact that they make great demands on the attention and reliability of the workpeople, it is usually very difficult and troublesome to discover the correct point of adjustment of such a cock. The " precision spinning machine " also constructed by L. Morane and described in French patent 12,545 (patent of addition to French patent 410,267) proved to be even less satisfactory. According to this patent a cylindrical filter is built into the supply pipe. The filtering surface of this filter is partially covered by a cylindrical plunger. As the pressure in the pipe rises through partial blocking of the acting portion of the filter this causes the plunger to drop and expose a further filtering surface. The mechanism is too complicated and awkward, and moreover it does not even theoretically solve the problem of ensuring a regular supply, as the plunger only acts when the increased pressure in the pipe is due to blockage of the filter. Should, however, the pressure rise for any reason whilst the filter remains unblocked the plunger should act in the reverse manner and slightly reduce the filtering surface, whereas in fact it does not do so but exposes more filtering surface whatever the cause of the increased pressure.

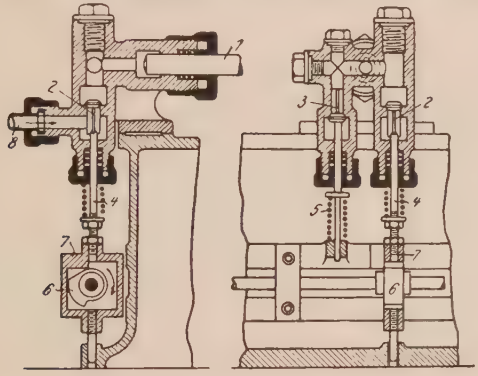
The problem was only solved by the introduction of spinning pumps for supplying the spinning solution.

Spinning Pumps. Originally, in the Chardonnet silk works, the spinning pumps which were interposed in the spinning solution supply pipes merely fulfilled the purpose of withdrawing the liquid from the collodium storage tanks, conveying it to the spinning nozzles and forcing it through these. To-day, the spinning pump also regulates the thickness and uniformity of the filament by regulating exactly the main controlling factor, namely, the rate of supply of spinning solution to the nozzle, by ensuring that the nozzle shall receive an exactly measured and uniform supply of the liquid per unit of time. This is now in fact the only function of the spinning pump in most cases, as the solution is conveyed to the spinning machine from the supply tanks either by compressed air or by interposed supply pumps, so that the spinning solution is supplied under pressure to the spinning pumps which form part of the machine.

These pumps may be divided into piston pumps and gearwheel pumps. Formerly, piston pumps were exclusively employed. When gearwheel pumps were first introduced, their simple and readily accessible construction, and the fact that they were capable of supplying solution at a far more uniform rate than the piston pumps of those days, caused them to be generally preferred, especially as they were, in addition, of simple construction and relatively cheap. When experience showed, however, that gearwheel pumps wore out much more rapidly than piston pumps, and therefore had a much shorter life, and after piston pumps had been constructed of more modern design, which greatly reduced the irregularities in their output, piston pumps came into favour once more, and to-day the tendency is to prefer them to the others. It is said, however, that it is difficult to construct piston pumps which are as tight as the gearwheel pumps.

Piston Spinning Pumps. Desmarais, Morane and Denis were the first to replace the simple pumps, which had until then been used for conveying the collodium spinning solution, by pumps with positively controlled valves. This occurred long before the construction of Morane's precision supply device already referred to.

Figs. 14A and 14B show the pump, which is described in German patent 197,167, Swiss patent 33,335, and French patent 342,655, in vertical section and plan. The spinning solution enters through the tube 8. The inlet valve is held in position by the spring 4. The valve rod is joined to the frame 7, which is moved vertically by the cam 6. The cam-shaft and the piston 1 are driven from the same source. The inlet valve 2 is lifted by the cam 6 as soon as the piston 1 has commenced its suction stroke, and returns into its seating at the moment when the compression stroke commences. The outlet valve is not regulated in this way but is only opened by the piston pressure transmitted through the liquid and returns to its seating under the action of the spring 5. The device does not regulate as exactly as its inventors presumably

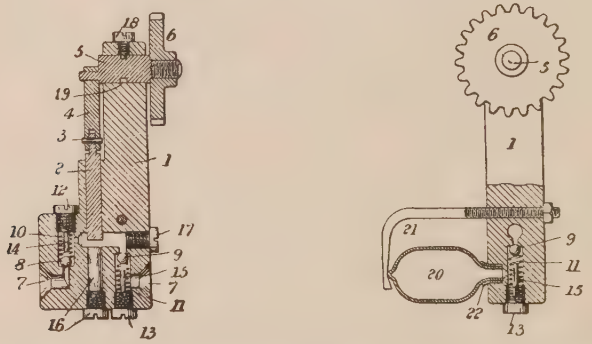


FIGS. 14A AND 14B. PISTON SPINNING PUMP OF DESMARAIS, MORANE AND DENIS

anticipated, and even the slightest leakage of the valves (for example, through intercepted insoluble particles) renders the whole action of the pump illusory. As there was only one piston the individual piston strokes were bound to cause constant fluctuations in the speed of flow of the spinning solution, and consequently in the size of thread. For these reasons the pumps were never used extensively.

Essentially the same disadvantages were shared by the pump described in Donnersmarck's British patent 16,605/1903, German patent 189,139, and Austrian patent 21,182, which is shown in Figs. 15A and 15B, although this pump is provided with a small wind-box (20) in order to equalize the pressure fluctuations. The spinning solution is forced under pressure into the inlet valve 8 of the pump. This pressure is, however, insufficient to open the outlet valve 9, which is kept closed by springs, weights or the like ; it is only opened by the pressure due to the piston 2, which is actuated by the revolving shaft 5, and the crank 4. The wind-chamber 20 communicates with the outlet. The entry of air into the pump is prevented by the pressure in the pump chamber. The component parts of the pump can be easily detached for cleaning or repairs and reassembled.

This pump is, moreover, of interest because it represented the first case in which each nozzle was served by a separate pump, as is now the almost universal practice, whereas formerly only one, or at most two pumps were attached to each spinning machine. This represented a distinct advance, which contributed greatly to the achievement of a uniform size of filament, as pressure variations which were previously caused by blocking or temporary disuse of individual nozzles were done away with. Moreover, the unavoidable pressure differences throughout the machine, caused by the use of a single



Figs. 15a and 15b. Piston Spinning Pump of Prince Donnersmarck

pump, and due to the fact that the nozzles farthest removed from the pump were necessarily under a lower pressure, were avoided. (It should be noted that in works employing the stretch-spinning process a single pump is often still employed to serve a whole series of nozzles.)

A pump very similar to the one just described is that patented by the Société Générale de Soie Artificielle, of Brussels, in British patent 5766/1905, and Austrian patent 25,175, which is also due to the same designer, Topham.

An essentially different type of piston pump from the small and relatively high-speed pumps just described is represented by the spindle cylinder pumps, in which a piston, mounted on a screw spindle in a wide cylinder, is slowly moved to and fro by the revolution of the spindle. Such a pump, constructed by Chas. C. Leclaire, is described in French patent 399,727, and shown in Fig. 16. In order to draw in the spinning solution through the supply pipe 12 and the opening 13, the spindle 3 is turned by the handle 11 in such a direction that the piston 2

moves from left to right. If then the part 9, which is united with the spindle is now coupled with the gearwheel 4 by liberating the spring 7 and the action of the hemispherical joint 8, the spindle is forced to turn in the reverse direction, as the gearwheel is actuated by 5 and 6 ; consequently the piston 2 travels from right to left and forces the spinning solution out through the aperture 13 and the pipe connection 10. The same principle is made use of in United States patent 732,784 of Ryon and Waite. A releasing mechanism for the pistons of pumps of this type is described by Lequeux in French patent 415,619.

These pumps were used in many works for a long period. They only very imperfectly satisfied requirements with regard

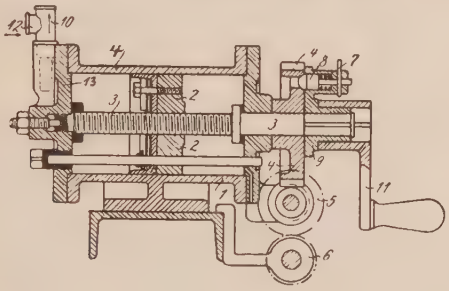


Fig. 16. Leclaire's Piston Spinning Pump

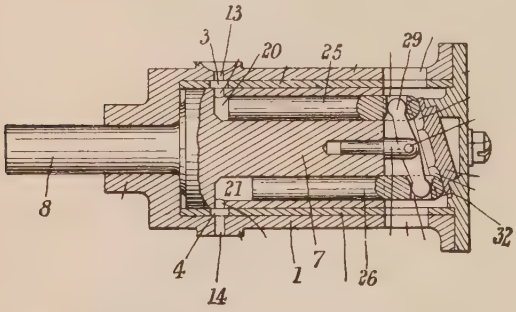
to uniformity and output, and were soon replaced by others of improved design.

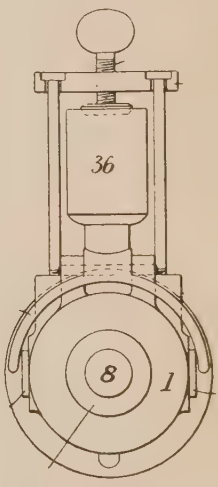
The first of these were high-speed multi-piston pumps. Such pumps were probably first constructed for artificial silk manufacture by Tetley and Clayton for S. Courtauld & Co. They are described in British patent 17,876/1907 from which Figs. 17A and 17B are taken.

The free space between the cylinder 7, driven by the shaft 8, and the casing 1, is divided into two chambers 3 and 4, by diaphragms. Chamber 3 forms the inlet chamber and chamber 4 the outlet chamber for the spinning solution, which enters the chamber 3 through the channel 13 and leaves chamber 4 through channel 14 and so passes to the spinning nozzle. Pistons 25 and 26 travel in the channels 20 and 21 which are connected with the chambers 3 and 4, and these pistons are linked by the lever 29, which is actuated by the revolution of the oblique plate 32, which is carried by the cover. Instead

of two cylinders four may be contained in cylinder 7. In this pump also a wind-box 36, is attached to the chamber 4.

Wind-boxes of the construction which we have several times referred to, which serve the purpose of equalizing the pressure fluctuations between the individual piston strokes, have the disadvantage that any small quantities of spinning solution which may find an entry are not automatically expelled, and that unless the mechanism is frequently cleaned, they accumulate in the dead space, finally coagulate, and may cause stoppages by means of loosened particles of coagulated material. More recently wind-chambers are so constructed that





Figs. 17a and 17b. Tetley and Clayton's Piston Spinning Pump

they are continuously traversed by the spinning solution during its passage to the nozzle. Pumps are also built without air-chambers, but, at any rate in the case of pumps with a limited number of pistons, say 2 or 3, an air chamber is absolutely necessary if a uniform filament is desired.

The quantity of spinning solution supplied, and, consequently, the calibre of the thread, depend in the case of piston pumps, mainly on the rate of motion of the pistons and, consequently, on the speed of rotation of the driving pulley, and can be adjusted to the weight of thread required by altering the driving gear. The control is carried out by first adjusting exactly the pressure within the pump, and then determining the quantity of liquid discharged through the nozzle either

gravimetrically or preferably volumetrically. It is incorrect to remove the nozzle for this test, as was pointed out by H. Jentgen.

With regard to the number of pistons, we have already seen that Tetley and Clayton's pump was provided with 2 pistons, but that provision was made in the patent for the use of four. However, more uniform action of the pistons is attained if their number is divisible by three, as is indicated by theoretical considerations. Consequently, pumps with 3, 6, or 9 pistons are preferred, but pumps with 2 and with 5 pistons are also constructed. According to E. Gerberich (*Kunstseide*, 1925,

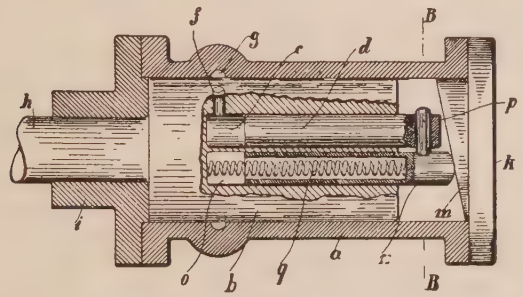


FIG. 18. HILLEBRAND'S PISTON SPINNING PUMP

page 98), the use of more than 3 pistons offers no advantage, as, for example, a 6-piston pump shows exactly the same percentage fluctuations as a 3-cylinder pump.

A spinning pump of this type constructed by P. Hillebrand and described in German patent 353,226, is shown in Fig. 18. It consists of the cylinder *b*, rotating in the casing *a*, and provided with several channels *c*, each of which holds a piston *d*. These channels communicate through the channel *f*, with the internal, divided circular groove *g*, which serves for the entry and exit of the spinning solution. The alternate communication of the pumping cylinders with the one or other portion of the circular groove is automatically regulated by the revolution of the cylinder *b*, which is attached to a shaft *h*, which is mounted in the inner cover *i* of the cylinder. On the inner side of the cylinder cover *k* an oblique cam-plate *m* is attached in the well-known manner. In this pump of Hillebrand the ends of the pistons *d* do not however engage directly with the cam-plate, but are actuated by the auxiliary pistons provided for each, with the help of the driver pins *p*. In this way it is arranged that pressures along the direction of their

axes only are transferred to the pump pistons, and not transverse pressures, and in this way heavy wear is avoided.

The Gesellschaft zur Verwertung Chemischer Produkte, Berlin, describe a piston pump, in German patent 359,999, in which the pistons are not directly coupled, but carry out their to and fro motions independently, being actuated by a curved guiding mechanism.

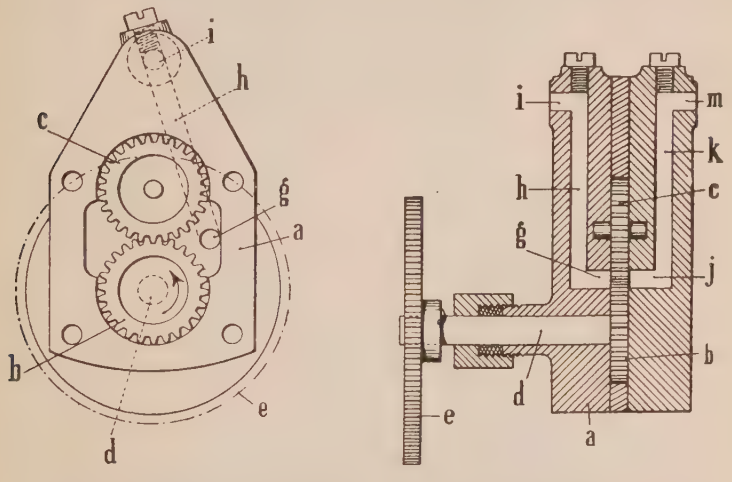
The newest type of piston spinning pump is probably that of Gerberich & Co., Mannheim, in which fluctuations in the discharge are very simply compensated by a doubly-acting auxiliary piston, working in the contrary sense, in such a manner that at each period of maximum pressure, due to the main pistons, the maximum counter-pressure comes into play, and so maintains the resultant pressure at precisely the desired level, so that the resultant pressure curve is practically a straight line. It remains to be seen whether this new, and perhaps rather too complicated, pump will prove satisfactory in practice.

Gearwheel Pumps. The well-known principle of gearwheel pumps is that two gearwheels, which engage exactly and are placed in a flat, closely fitting chamber, force a liquid filling one of the halves of the chamber into the other half when the gearwheels are revolved, so that it is only necessary to provide a tube to carry the solution into the one half and a discharge tube on the other half, in order to effect a constant and uniform transference of the liquid on rotating the gearwheels. Such pumps had previously been used for manufacturing purposes, for instance, as oil pumps for lathes and the like. Their use for conveying spinning solutions for artificial silk is first mentioned in British patent 28,320/1912, French patent 450,906 and Belgian patent 251,256 by F. Küttner. The patentee mentions the following advantages of gearwheel pumps as compared with piston pumps: perfectly uniform conveyance of the spinning solution to the nozzles ; consequent production of an extremely uniform thread, and intensive kneading of the spinning solution by the gearwheels immediately before spinning, whereby the mass attains a high degree of uniformity, which favourably influences the quality of the thread. Finally, gearwheel pumps are alleged to be simpler and cheaper than piston pumps, to require no packing and no valves and to be more easily taken to pieces and cleaned.

Küttner's pump is shown in two sections at right-angles (Figs. 19A and 19B). Casing *a* contains the two gearwheels *b* and *c*, which engage with one another, and of which *b*

is revolved by the shaft *d* and the driving wheel *e*, and in turn drives the gearwheel *c*. The spinning solution enters through the inlet *i* which is connected with the storage tank, the channel *h* and the opening *g* into the chamber shown to the right of the gearwheels in Fig. 19A, and is carried by the gearwheels to the left-hand side, passing on through *j*, *k*, and *m* to the spinning nozzle.

The quantity of spinning solution conveyed in unit time by gearwheel pumps naturally depends on the speed of revolution,

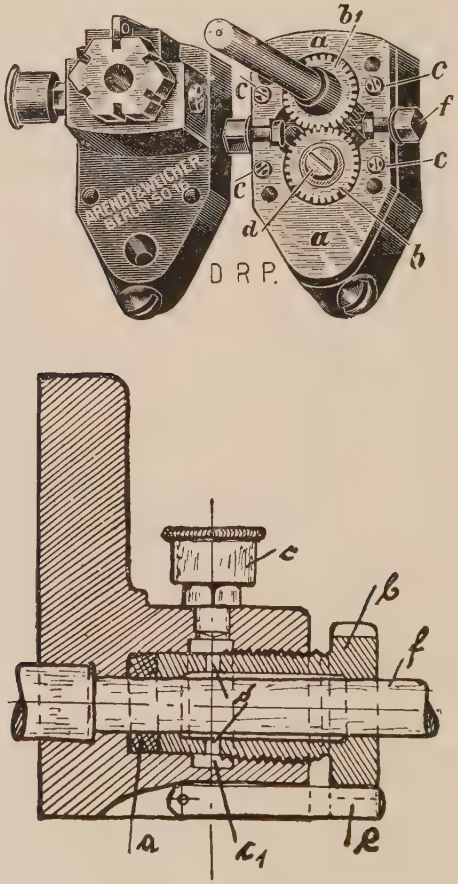


FIGS. 19A AND 19B. KÜTTNER'S GEARWHEEL SPINNING PUMP

and can be adjusted by altering this speed, but only within certain limits, as too high a speed causes very rapid wear of the pump. These pumps are, therefore, mainly regulated by the choice of a definite length of gearwheel cog on which the quantity of liquid conveyed is naturally dependent. Thus, for instance, according to the desired width of thread, pumps with a height of gearwheel cog of 4, 6, 8, 10, or 12 mm. are used. The control of the output of the pump is carried out exactly as for piston pumps.

In a recent year, Arendt and Weicher, Berlin, placed a new gearwheel pump on the market, which is said to effect a very uniform delivery and to have a relatively long life. These

results are achieved mainly by the possibility which this pump offers of adjusting one of the gearwheels *b* (Fig. 20A) and the centre plate *a*. Thus it is possible to adjust the two conveying



FIGS. 20A AND 20B. ARENDT AND WEICHER'S GEARWHEEL SPINNING PUMP

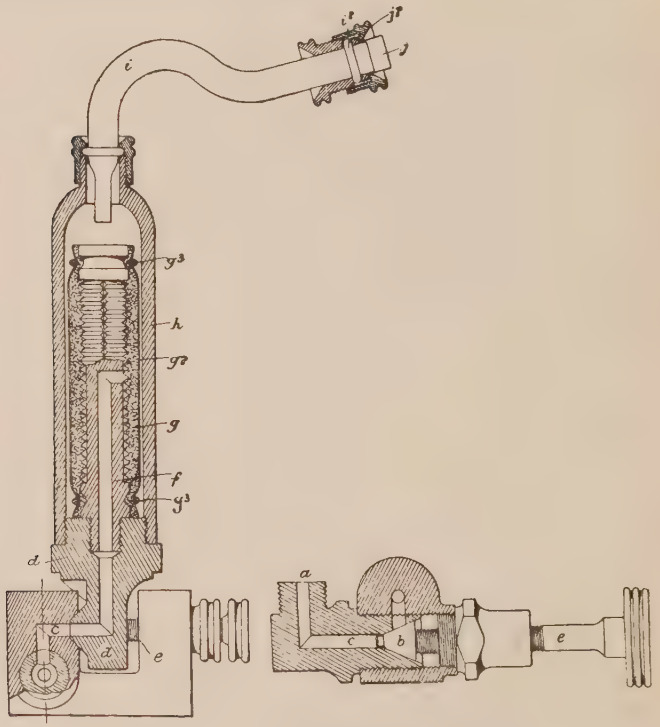
gearwheels so that they may engage accurately with one another and with the surrounding plate, by which means slight leakages, which affect uniform delivery, can be easily avoided, and the renewal of the centre plate is seldom necessary.

The lubrication of the front driving shaft *f* (Fig. 20B) is greatly improved by placing the packing *a* well within the pump casing, so that a long cast iron stuffing box *b*, which is easily replaceable, may serve as a bearing for the shaft. Fig. 20A shows this pump after removal of the upper portion, and Fig. 20B the mounting and lubrication of the driving shaft.

Spinning Filters. When discussing filtration of the spinning solution we already mentioned that the most careful filtration before supplying the solution to the spinning machine is usually insufficient to prevent blockage of the nozzles through insoluble particles, because the possibility exists during the long travel through the supply pipes that the solution may again be contaminated by insoluble particles which are derived from corroded piping, decomposed remains of old spinning solutions and so forth. It is, therefore, necessary to pass the spinning solution through one or more further filters before it arrives at the nozzle. These filters are preferably placed on the spinning machine itself, and special filters are preferably mounted for each nozzle. It is convenient firstly to provide a large plate filter of quadrilateral or oval shape in each side tube leading from the main supply tube to the individual nozzles or groups of nozzles. This filter is constructed similarly to the individual chambers of a filter press, and provided with similar filtering material. Frequently, however, no filters are used at this point, and filtration is confined to the provision of a smaller filter at the end of the supply piping between the nozzle and the nozzle tube; this ordinarily takes the form of a so-called filtering candle of the very ingenious and practical construction of Chas. F. Topham, which is described in British patent 23,157/1900, German patent 125,947, Swiss patent 24,301 and U.S. patent 702,382.

Figs. 21A and 21B show the arrangement of such a filtering candle. The spinning solution enters through the regulating valve *b* and the channel *c* into the body of the filter *f*. This consists of a cylindrical filter candle provided with longitudinal and transverse ridges and with a central boring which passes from the channel *c* to about the middle of the candle. It is here in communication with a similar channel, through which the spinning solution passes to the outer surface of the candle and is distributed along the longitudinal and transverse corrugations. The candle *f* is wrapped in a filtering layer consisting of cotton

fabric or the like, through which the spinning solution passes before entering the inner chamber of the casing *h* which surrounds it, and from there through the glass tube *i* to the nozzle *j*. The whole filter casing, with the nozzle, is pivoted by the joint *d* in a special section of the



FIGS. 21A AND 21B. TOPHAM'S FILTER CANDLE

supply channel *c*, so that the nozzle can be readily removed and re-inserted into the spinning bath by swinging the whole arrangement round.

A very similar filter candle is described by J. C. Hartogs in German patent 257,144, and is provided with helical, uniformly ascending outer channels.

A similar filter candle is described by W. P. Dreaper in German patent 414,675, in which the spinning solution is forced in the reverse direction, viz., from without to within. Fig. 22 shows a vertical section of this candle ; the spinning solution enters by the inlet tube *b* and the channel *c* into the annular space between the casing *a* and the candle *h*, which is united with the casing by the screwed joint *d* ; from this space the spinning solution is forced through the filtering material and

the transverse channels j to the central channel i, from which it passes directly to the nozzle f which is affixed to the headpiece e. In this arrangement the filtering medium is pressed more firmly against the candle when the pressure is increased, and not driven away from the candle, as in Topham's arrangement. It is stated that in all cases a more complete filtration is obtained.

Filtering candles are ordinarily used, even when a large plate-filter is inserted in the supply pipe to each nozzle, as already described.

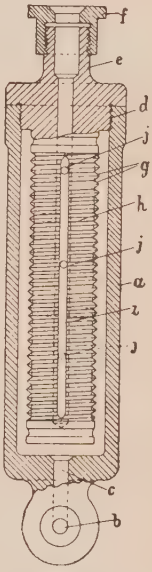


Fig. 22. Dreaper's Filter Candle

After this filtration the spinning solution is usually passed through a small filter plate on the actual nozzle, immediately in front of the outlet. In the collodium process this is filled with silk (Müller gauze), in the cuprammonium process with fine iron gauze, and in the viscose process with nickel gauze, or with cotton fabric or batiste.

Spinning Nozzles. The artificial silk thread as we see it on the spools or reels, or on the knitting or weaving loom, always consists of a bundle of more or less numerous fine filaments. In speaking of artificial silk thread one must, therefore, distinguish between individual filaments and the main thread. As in the case of cotton wool or other yarns, the threads which are finally used may, of course, in turn, be formed of several twisted main threads.

In producing the thread, a single filament is naturally formed at each spinning nozzle. This filament is usually too weak, particularly when moist, to be conveyed through long distances, treated, and wound. Therefore, several individual filaments are united to a main thread as soon as possible after they are produced. A nozzle from which the spinning solution is forced during spinning has either a single opening and thus yields a single filament, or is provided with a number of openings equal to the number of individual filaments in the main thread. A distinction is thus made between single nozzles and multiple nozzles.

When spinning with single nozzles, these must be grouped

in numbers corresponding to the number of filaments in a main thread. A single nozzle is shown in Fig. 23. The single nozzles belonging to a common group are usually attached to the side tubes of a common supply tube, which is frequently constructed of glass and forms a so-called spinning comb. The single nozzles themselves are also usually constructed of glass and are connected with the side tubes by a piece of india-rubber tube. Spinning with single nozzles offers certain advantages. Each individual filament can be observed, and each nozzle can be replaced if, for instance, it is obstructed, without interrupting

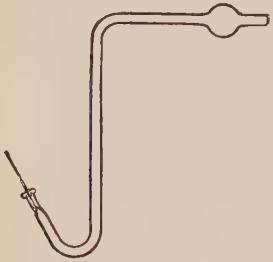
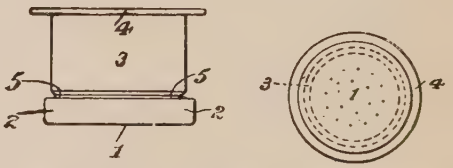


Fig. 23. Single Spinning Nozzle



Figs. 24a and 24b. Multiple Spinning Nozzle

the work of the other nozzles, so that the main thread is not interfered with. These spinning combs often offer the disadvantage that the pressure is not equal at all parts of the system, but is, on the other hand, higher at the first nozzle than the last. According to Franke and Müller (British patent 4080/1911, and German patent 250,595), this disadvantage can be overcome by providing the supply tube for the spinning solution with a bulb-shaped expansion in front of the spinning nozzles, to which the funnel-shaped capillary tubes are attached. It is stated that in these expanded bulbs the pressure is always prefectly uniform.

In multiple nozzles, each nozzle has as many apertures as the number of individual filaments in the main thread. Thus, each multiple nozzle supplies a main thread. Multiple nozzles are usually constructed of metal, such as silver, nickel, platinum, gold-platinum alloy, gold-palladium alloy, and so forth and take the form of small cylindrical caps with a flat edge,

the floor of which is provided with the small spinning apertures, and each may, for example, have the cross-section shown in Fig. 25 (see also the nozzles in Figs. 24A, 24B, and 26). These caps are affixed to the end of the nozzle tube by means of a screw cap which overlaps the rim, and which is usually constructed of ebonite in the manner, for example, which is shown in Fig. 13, page 87.

In French patent 16,058 (additional to 436,556), Boissor proposes a kind of bayonet joint with a stirrup which slides on a rising plane, for fastening the nozzle, which consists of a perforated disc.

With regard to special screwed joints for attaching nozzles to spinning tubes, see German patent 390,742.

Nozzles of this type, consisting of a simple plate or disc provided with apertures, which are attached to the supply tube by screw caps, are described by the same inventor in French patent 436,556 and patent of addition 15,925.

P. Burill has also described a nozzle in French patent 442,632, which consists of a simple perforated plate of platinum, nickel, or acid-proof ferro-silicon alloy sealed into the end of a glass tube.

According to British patent 30,306/1910, G. Guadagni employs a spinning nozzle consisting of a ground plate with the necessary number of perforations 4 mm. wide, and of glass spinning capillaries which are inserted into these perforations and made tight with a layer of vulcanized rubber. These capillaries can be interchanged as often as necessary. Individual capillaries can be replaced by solid rods, in which manner the number of filaments can be correspondingly reduced.

A. Latapie (French patent 431,096) proceeds in a very similar manner by embedding a number of glass capillaries, arranged in a circle, in a binding material, which hardens and so forms one mass with the capillaries ; but his capillaries are not interchangeable. As the embedding material he can, for example, use cement with an acid-proof coating, gutta-percha, and paraffin ; or a mixture of india-rubber, tallow, slaked lime and red lead, or cement with asbestos and water-glass ; or, finally, an acid-proof alloy, e.g. lead and bismuth, or the like.

The nozzles described by Buffard, in French patent 442,630, and by Girard and Buffard in French patent 445,783, are very similar in principle. According to the first patent, capillaries of glass or of resistant metal, of a definite shape, are cemented together by cement or other binding material. According to the second patent, small plates, each provided with one perforation, are fastened into the openings of a ground-plate of acid-proof material and fixed with cement.

In German patent 360,000, R. Kühnel describes a nozzle of base metal, in which bodies of a noble metal provided with spinning apertures are inserted, which form one plane with the surface of the spinning nozzle and are no thicker than the thickness of the body of the nozzle. This nozzle is shown in Fig. 25. Other forms of nozzle with perforated plates are described in P. Girard's British patent 5386/1912, German

patent 266,140, French patent 438,131 (and patent of addition 15,399), U.S. patent 1,164,084, and Belgian patent 243,409; and also in A. Pellerin's French patent 442,022.

In British patent 18,965/1912, J. E. Criggal asserts that the existing nozzles of pressed platinum foil—i.e. the platinum caps which we have already described—suffer from the disadvantage that the perforated floor is not sufficiently thin and uniform to enable fine and uniform apertures to be produced, and that, on the other hand, the rest of the cap is not strong enough to be satisfactorily fastened into the delivery tube. He has, therefore, designed a nozzle consisting of two parts. It consists of a very thin and very uniform nozzle floor (1), (Fig. 26) provided with the spinning apertures, and the much thicker nozzle ring (4 and 5). These parts can be manufactured of any resistant metal or metallic alloy; e.g. the perforated portion can be constructed of platinum and the other portion of a cheaper metal. The two parts are inter-connected by bringing the flanged edges (2 and 6) of each part together and doubling them over together, as shown in Fig. 26.

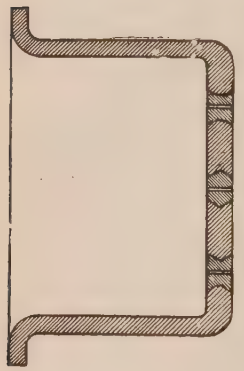


Fig. 25. Kühnel's Spinning Nozzle

A special kind of spinning aperture is described by J. L. Laroche, in French patent 459,849. The perforations are bored in glass or similar material in such a manner that they have a comparatively wide cross-section on the inside of the nozzle, which is gradually contracted until it finally forms a narrow cylindrical channel.

The width of the nozzle apertures varies greatly according to the product to be produced. For the production of silk of average quality by the ordinary spinning process, for example, apertures of 0·05 to 0·1 mm. are employed. Under otherwise identical conditions the thickness of the thread would naturally correspond to the nozzle aperture. But this is not the only factor which decides the thickness of the thread, so that it is not possible to say that finer nozzle apertures must necessarily be used for finer filaments. In producing the very finest filaments by the stretch-spinning process comparatively wide apertures of 0·25 to 0·5 mm. are actually generally used. The great fineness of the filaments is in this case obtained by the extreme degree of stretching of the filament.

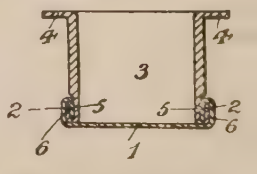


Fig. 26. Criggal's Spinning Nozzle

A nozzle is described in German patent 168,830 and Austrian patent 28,581 by Soc. Linkmeyer, in which the filament, on being discharged from the nozzle aperture, is immediately surrounded and conveyed by a tube-shaped stream of spinning bath liquid. Fig. 27 shows the arrangement in longitudinal section. Between the lower cone-shaped end *d* of the nozzle *a*, and the edge *e* of the aperture of the container *c*, there is provided an annular space *f*, through which the spinning bath liquid which enters from the container through *g* is discharged and then surrounds and conveys the filament *b* which is discharged from the nozzle.

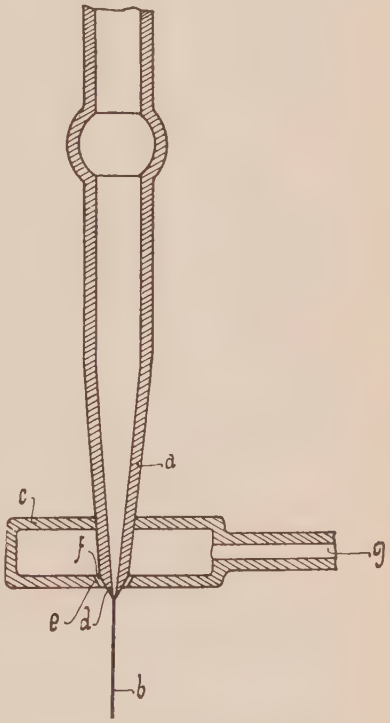
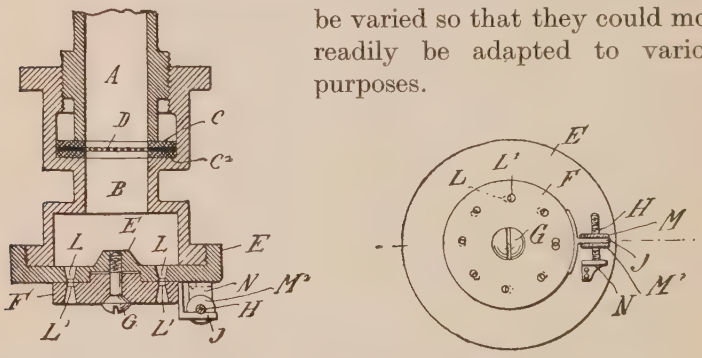


Fig. 27. Spinning Nozzle of Soc. Linkmeyer

A special method of producing fine spinning apertures in glass nozzles is described in German patent 96,060 of Dr. A. Nobels Sterbhus, and also in U.S. patent 988,424 of C. Woegerer and French patent 442,631 of Chas. F. Buffard. The principle of all these processes is that fine metal wires are sealed into the glass and then dissolved in acids, so that a fine capillary channel remains. The individual working details described in the above patents differ slightly. According to Belgian patent 168,556, R. Hömberg obtains nozzle apertures of any desired cross-section in a similar manner by sealing metal wires of annular, sinuous, flat, or other cross-section into a glass matrix. Details of the production of the fine metallic wires, for example of platinum, required for this process, and the necessary

draw-plates for these, are given by K. Süvern (*Kunststoffe*, 1916, page 5). Further literature relating to this subject will be found in Muspratt, *Handbuch der technischen Chemie*, 4th Edition, Vol. 4, page 303 ; E. Oberg, *Scientific American*, 1913, page 186 ; German patent 16,936, French patents 397,943, 421,676, 437,770, and U.S. patents 810,503 and 810,504.

The nozzle aperture constitutes one of the variable factors which affect the thickness of the thread. It was, therefore, natural that attempts were made to construct nozzle apertures the cross-section of which could be varied so that they could more readily be adapted to various purposes.



Figs. 28A and 28B. Bernstein's Spinning Nozzle

The nozzle described by A. Bernstein in German patent 216,391 and shown in Figs. 28A and 28B belongs to this class. It comprises two plates E and F provided with circular perforations L and L^1, of which the larger plate E is fixed, whilst the smaller F can be revolved. The apertures are of comparatively wide cross-section, for example, 2 mm. When the openings coincide they form a cylindrical passage through the two plates. If, however, the upper plate is revolved slightly by means of the contrivance comprising the pin J, the screw H, and the screw heads M and M^1, the apertures are relatively displaced and the passages become progressively smaller at the junction of the two plates. A similar reduction of the nozzle apertures is effected in the nozzle of Rents and Eilfeld, described in German patent 221,572, by throttling the nozzle apertures, which are cone-shaped and expand inwardly, by

cone-shaped needles which can jointly be adjusted and which abut on one wall of the apertures. The plate which carries the needles can be raised or lowered by an eccentric which is connected with the indicator of a scale outside the nozzle. Any adjustment of the indicator alters the position of the eccentric, and thus moves the plate carrying the needles upwards or downwards, causing the points of the needles to slide along the walls of the narrow apertures and so to alter the effective diameter of these.

The Société de la Viscose, Paris, describe in their French patent 345,343 a spinning head with an interchangeable spinning disc. The spinning apertures are formed by grooves which are cut into a fitting of glass or hardened steel, which is held by a metal holder. These grooves taper towards the point of the spinning head. It is said to be very easy to cut the spinning apertures with complete uniformity, and also that the contrivance can be very readily cleaned after removing it from the holder. Above the spinning plate a filter sieve is fitted for the final purification of the spinning solution. In a spinning machine described by E. Mertz, in Swiss patent 34,741 and French patent 364,912, the spinning apertures are similarly formed by channels which are cut longitudinally on a conical plug and which are bounded by the seating of the plug, the lower end of which rests on an india-rubber cushion. Should the spinning apertures become blocked, it is only necessary to depress the plug. In consequence of its conical shape, a broad annular space is thus formed between it and its seating, through which the spinning solution can escape and wash away the impurities causing the stoppage. In the same patent specification a nozzle is described in which the spinning aperture or apertures are arranged at the lower, infolded extremities of glass tubes, which are attached to the supply tubes by a suitable fitting (see Fig. 29). Impurities, or air or gas bubbles, are said to collect in the annular space above the spinning aperture.

Fig. 29. Mertz Spinning Nozzle

Various materials have already been mentioned, of which

nozzles may be constructed. Glass and platinum nozzles were formerly used almost exclusively, and have so far proved to be the best, particularly the platinum nozzles. Nickel and silver nozzles have not proved satisfactory. Gold-platinum alloy is also quite suitable, but jets prepared from it require care during heating for cleaning purposes on account of the lower melting point. Gold-palladium alloy appears to be better. On the other hand, molybdenum (German patent 331,513 and French patent 506,787) and tantalum—which has been tried experimentally—have not proved suitable. This is also true of the talc nozzles, patented by Glanzfäden A.-G., Berlin, in German patent 310,743, which are stated to be as good as platinum or glass nozzles, but to cost only about one-tenth the price of platinum nozzles and about one-fifth of that of glass nozzles. The use of phenol-formaldehyde condensation products as a constructional material for nozzles was patented by the Sudenburger Maschinenfabrik and F. H. Meyer in German patent 361,735. They also patented the manufacture of such nozzles in German patent 344,327.

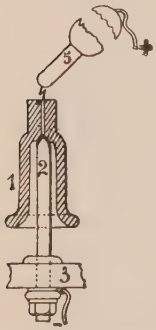


Fig. 30. Denis Nozzle Cleaner

A special method of cleaning the capillaries of glass nozzles is described in M. Denis's German patent 263,786. It consists in passing an electric spark through the capillary, which is said to remove the obstructing foreign bodies by melting, combustion or volatilization. Fig. 30 gives a diagrammatic representation of the process. The glass jet 1 to be purified is placed on the metal point 2 of the stand 3, connected with one pole of an induction coil, whilst the metal point 5, which is connected with the other pole of the coil, is approached to the capillary of the jet, by which means a spark passes through the latter and cleans it.

E. Schülke also constructed a contrivance for purifying spinning jets. It is described in German patent 342,536, and shown in Fig. 31. According to the patent specification the arrangement and method of working are as follows: The jet

to be cleaned, for example a bakelite plate, is inserted in the holder 2. The lever 3 is then depressed. This actuates the piston 4, which transfers the pressure through a strong spring 5 to the hollow cylinder 6. This cylinder 6 carries at its lower end the india-rubber mouthpiece 7 and is maintained in its

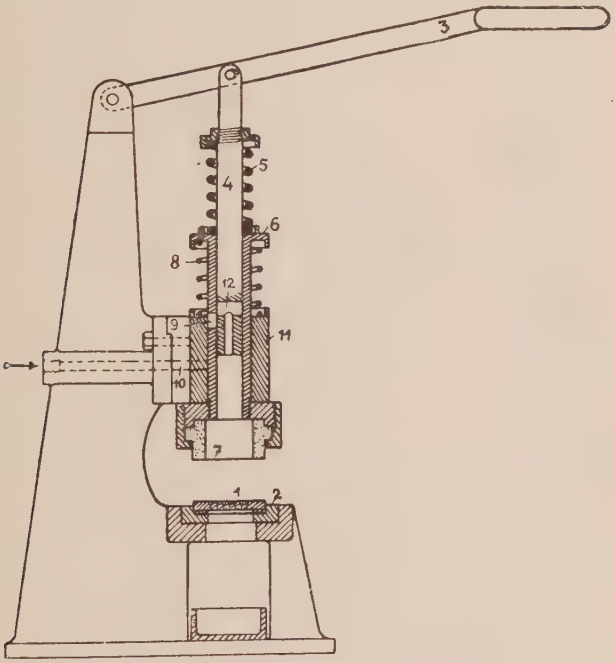


Fig. 31. Schülke Nozzle Cleaner

normal position by a weaker spring 8. On depressing the lever 3 the spring 8 is compressed until the mouthpiece 7 comes into contact with the nozzle 1. In this position the lateral bore 9 in the hollow cylinder 6 coincides with the outlet 10 for the high pressure water in the outer cylinder 11. The high pressure water supply can only pass when the lever 3 is depressed and, therefore, depresses the piston 4, the transverse boring 12 of which permits the water to pass, which had previously been cut off from the rubber mouthpiece by the piston 4. On releasing the lever, the inner piston 4 first ascends, and the high

pressure water supply is thus cut off before the nozzle is liberated. Below the nozzle a flat dish filled with water is placed, which receives the fine streams of water which penetrate it. It is thus possible to observe when the individual apertures are cleared. High pressure air can be used instead of water.

The contrivance enables the work to be carried out with very great rapidity, and prevents the breakage of the glass nozzles by the workpeople, which is so frequent when complicated holding contrivances are used. The holder 2 may be interchangeable, so that jets of any size and construction may be accommodated.

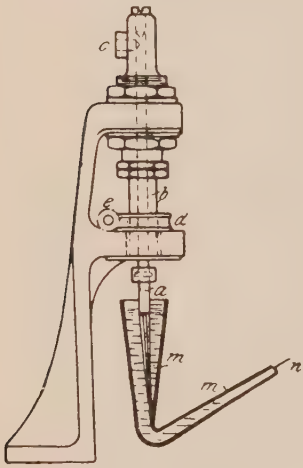


FIG. 32. STREHLENERT ROTARY NOZZLE

Revolving Nozzles. The object of using revolving nozzles, namely, immediate twisting of the thread—has already been mentioned when considering the spinning process. Apart from twisting the thread, this method of operation also offers the advantage that any ruptured individual filaments are twisted together with the main thread and do not become dispersed in the spinning bath, in which case they reappear later as faults in the threads and have to be specially removed.

Revolving nozzles have not found any permanent use in practice. They require a fairly complicated apparatus and produce undesirable eddies and currents in the spinning bath which cause frequent rupture of the thread, and, moreover the twisting effect is often very uneven. The employment of revolving nozzles has, therefore, ceased entirely, more especially because in the interval the problem of direct twisting during the spinning process was solved in a much more satisfactory manner by the centrifugal spinning machine.

The first revolving nozzles are described by R. W. Strehlenert in British patent 3832/1897, German patent 96,208, Swiss patent 13,695 U.S. patent 702,163 ; and in the patents of addition, British paten

58/1899, German patent 101,844, Swiss patent 17,950, and German patent 102,573.

Fig. 32 shows the considerably simplified apparatus described in the first patent of addition, German patent 101,844. The spinning solution is led to the nozzle *a* through the aperture *c* and the channel *b*. The nozzle *a* is revolved by the helical gearing *e* and *d*. The thread is carried down by the circulating spinning bath *m*, which passes through the elbow tube, and issues from it at *n*. A revolving nozzle which is similar

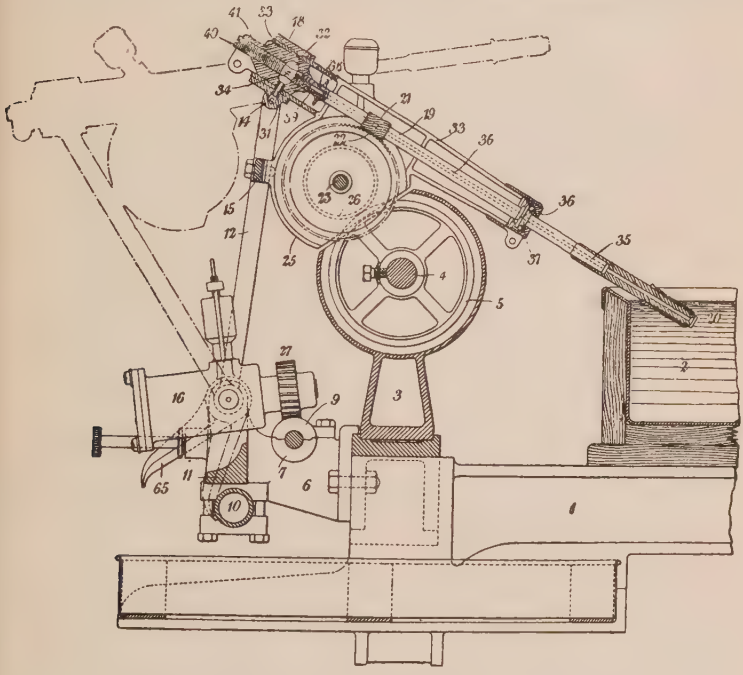
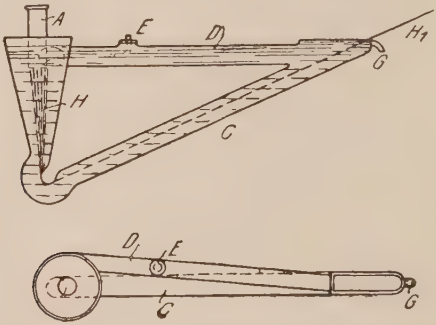


Fig. 33. Rotary Nozzle of Tetley & Clayton

n principle, but differently constructed, is described in British patent 17,152/1904, German patent 164,321, and French patent 345,274 of the Soc. de la Viscose. It is shown in Fig. 52, which represents a spinning machine of this firm. In these machines, the spinning head is directed downwards, and the thread therefore at first travels in that direction. On the other hand, in the arrangement patented by Linkmeyer in German patent 249,002, the nozzle is directed upwards.

Fig. 33 shows a revolving nozzle constructed by Tetley, Clayton, and S. Courtauld & Co., which is protected by British patent 19,157/1908, German patent 236,242, U.S. patent 979,434, and French patent 406,344. The iron frame 1 carries the spinning bath container 2. It also carries the support 3, for the driving shaft 4, with the friction pulley

5 and the support 6, of the driving shaft 7, which latter actuates the spinning pump 16, by the helical gear wheels 9 and 27. The spinning solution is supplied through tube 10. 11 is a fitting on the stand 6, with bearings which carry the rocking frame 12. 18 is a holder for the end of the casing, with bearings for one end of the spindle 19, which carries the nozzle 20 at its other end, and is actuated by the screw 21, driven by gear wheel 22 and shaft 23, which is in turn actuated by the wheel 5, driving the friction pulley 26. 25 is the casing surrounding the driving mechanism. The spinning solution passes from the pump 16, which is provided with an air-glass, through the opening 31, chamber 32, and



Figs. 34A and 34B. Strehlenert Eddy Nozzle

the lateral openings 34, and finally through the boring 35 of the spindle to the nozzle.

Strehlenert attempted to solve the twisting problem in another manner by using a stationary nozzle, whilst producing an eddying effect in the spinning bath by leading the inflowing bath tangentially into the funnel-shaped precipitation vessel as is shown in Figs. 34A and 34B. (See British patent 28,364/1902, German patent 102,573, Swiss patent 17,950, German patent 143,763, and U.S. patent 716,138.) In this arrangement it is difficult, if the thread breaks, to return it to the winding spool.

The same principle is followed by E. W. Friedrich (British patent 17,381/1905, German patent 172,264, Austrian patent 30,705, Swiss patent 35,080, U.S. patent 827,434, French patent 357,172), with the only difference that he produces an eddying motion in the spinning bath by spiral channels in the inner wall of the cylindrical spinning bath container.

The arrangement described in German patent 276,082 of R. Mewes is also a form of revolving nozzle. The rotary container which holds the spinning solution is provided with lateral jet-shaped or sieve-like openings, through which the spinning solution is extruded during rotation by the action of centrifugal force. It is stated that the extrusion can also be effected when the drum is at rest by causing the mass inside the drum to revolve centrifugally. This complicated arrangement was not, of course, adopted in practice.

There was a very interesting attempt by R. Mewes (German patent 252,841) to replace spinning nozzles by rollers provided with fine grooves. The apparatus consists, for example, of two superposed rollers firmly pressed together, with fine grooves, which are both half-surrounded on one side by the container holding the spinning solution, which fits closely to the rollers, so that only one side of these dips into the spinning solution.

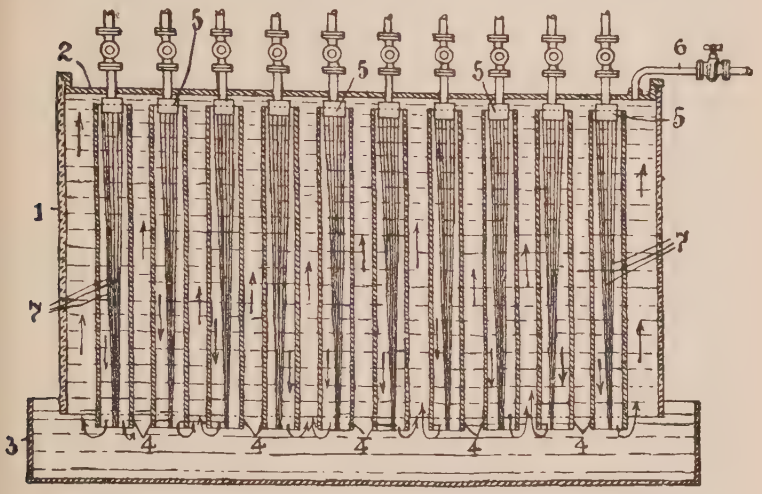


FIG. 35A. LINKMEYER'S SPINNING BATH
FRONT ELEVATION

When the rollers are revolved the spinning solution is supposed to be prevented from escaping between the flat surfaces, and only to escape to the other side through the fine grooves, from which it is withdrawn in the form of filaments. The spinning solution must have the consistency of a plastic mass, so that the threads are more or less rolled. Precipitation is out of the question, so that the process is a form of dry spinning. Very fine filaments cannot, of course, be formed in this way, but at the most a form of artificial horsehair might be produced. On the other hand, the dry spinning process is difficult or unsuitable for such thick threads. Finally, the circumstance that the surfaces of the rollers between the grooves would be soiled by the spinning mass would presumably make it impossible to

form satisfactory round threads in spite of the pressure between the rollers. In any case, the process has not achieved any practical importance.

The baths in the form of a suspended liquid column mentioned on page 82, took the form either of narrow tubes, attached above to a funnel, or of wide containers, usually cylindrical, which were sealed airtight above and which were filled with the precipitating liquid and dipped into a vat also filled with the same liquid.

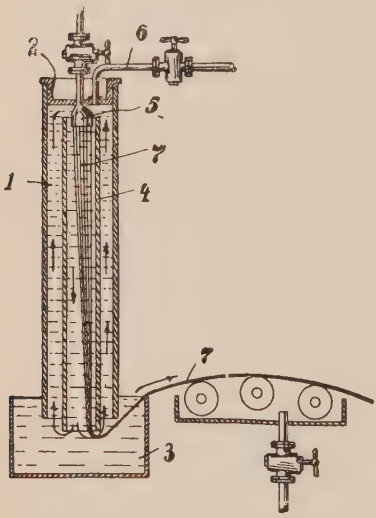


Fig. 35B. Linkmeyer's Spinning Bath. Side Elevation

Such apparatus has been described, for example, by E. Thiele, in British patent 16,588/1903, German patent 148,889, Austrian patent 18,082, Swiss patent 29,680, U.S. patent 750,502, and French patent 334,507 ; and in patents of addition—British patent 16,078/1906, German patent 178,942, Austrian patent 31,788, Swiss patent 35,436, U.S. patent 838,758 and French patent 367,980 ; and also by R. Linkmeyer in German patent 222,131. The apparatus protected by the last-named patent is shown in Figs. 35A and 35B. A vessel 1, which can be evacuated through pipe 6, and which is closed tightly above by the cover 2, dips into the liquid in the container 3. This vessel contains tubes 4, which are open above and below. The spinning nozzles 5 project into the tops of these tubes, and the bundle of filaments 7 is carried downwards, and after leaving the spinning bath is carried over guide rolls and thread guides to the winding contrivance. Similar apparatus is described by Crombie and Schubert in British patent 24,922/1908, and French patent 409,387 ; and by Ping and Schubert in British patent 22,635/1911. An arrangement by Thiele is described in German patent 148,889, and shown in Fig. 36 ; it consists of a funnel *b*, closed above, into the upper part of which the nozzle *a* and the supply tube *e* for the precipitating liquid enter ; and also of a tube *d* jointed to the filter *b*, through which the thread is led to the spool *f*. These processes are too complicated and impracticable for industrial purposes, more particularly if in addition, as in the apparatus of Crombie and Schubert, the process is to be carried out with two different precipitation

fluids in supernatant layers, the upper one of which has a rapid and the lower a slow action.

Guidance of the Thread. From the spinning nozzle the thread or bundle of threads passes either directly, in the dry spinning process or, after passing through the precipitation bath, in the wet spinning process, over one or more guides to the winding contrivance. The direction in which the thread or thread bundle is removed from the nozzle varies much with the spinning machine. Practically all possible directions have been used in practice : vertically from below upwards, or from above downwards ; obliquely upwards ; horizontally, and so forth ; or, finally, obliquely or horizontally guided threads may be passed through the spinning bath in a transverse or longitudinal direction. The latter arrangement is very often used in centrifugal spinning machines. It offers the advantage that the path traversed in the bath can be made as long as desired, and that the thread can be made to progress in the direction of the current in the flowing bath, and therefore meets with less resistance.

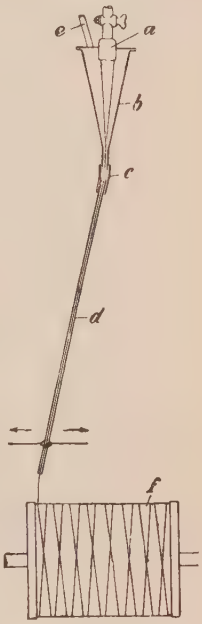
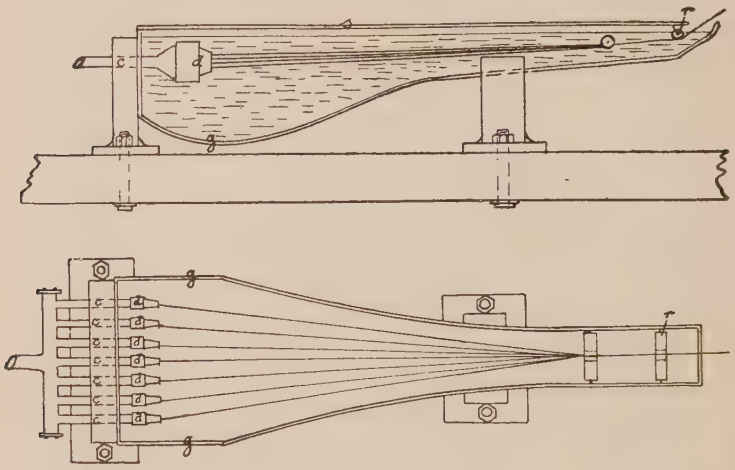


Fig. 36
Thiele's Spinning Mechanism

The arrangement described by F. Cochius in British patent 9,017/1903, German patent 163,293, French patent 331,404, Austrian patent 24,975, and Swiss patent 34,222, and which is shown in Figs. 37A and 37B, is very practical. The spinning solution is introduced through the tube *c* and the nozzle *d* at the front side of the container *g* ; from the nozzle the thread passes out of the spinning bath over the guide rolls *r* to the winding contrivance. In order to prevent the escape of solvent vapours as far as possible—more particularly in the case of collodium silk—the container may conveniently be covered by a glass plate *s*.

Thread guides usually consist of short or long rods constructed of glass, glazed porcelain or enamelled metal wire,

which are shaped into a fork, loop, hook, or spiral ring at their free ends. They must be perfectly smooth in order that the thread may pass over them without damage. Glass is, therefore, really the best material for this purpose, but with this material care must always be taken that it does not become roughened through the action of acid or alkali in the course of time, in which case the thread guide must be replaced. As



FIGS. 37A AND 37B. COCHIUS SPINNING MECHANISM

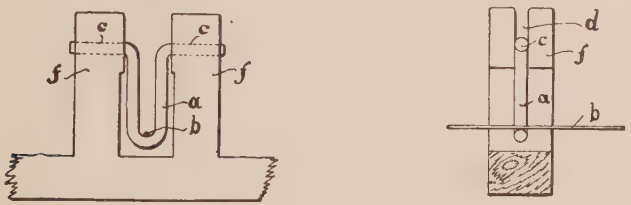
the artificial silk thread must not always be wound on to the winding spool at the same point, but this latter must be wound in a particular fashion, the thread guide adjacent to the winding spool usually has imparted to it an oscillating motion, unless, as in some centrifugal spinning machines, the winding arrangement itself, that is, the centrifuge, carries out the necessary to and fro motion.

If the thread guide moves so slowly that the winding spool makes many revolutions during one of its strokes, the thread windings will lie close to one another, and one obtains parallel winding. If, on the other hand, the thread guide moves so rapidly that the winding spool makes a few revolutions only during one stroke of the same, cross-winding results, as is shown for example in Figs. 36 and 44.

A special form of thread guide is shown in Figs. 38A and 38B, and is described by the Hölkenseide G.m.b.H., in German patent 361,970 ; it is intended to be used in place of the thread gutter described below. The thread *b* passes over the thread guide *a*, which is suspended on the stand *f* by its upper arms *c* and which has therefore a considerable amount of play in the direction of withdrawal of the thread. The thread is thus subjected to very little wear and can easily be removed from or replaced in the thread guide.

An arrangement which serves to place the thread under any required tension is described by L. Fivé in German patent 200,824.

According to British patent 4596/1913, French patent 451,913, and Belgian patent 247,209, P. Girard avoids the uneven tension of the fibre between the last thread guide and the preceding stationary thread



FIGS. 38A AND 38B. THREAD GUIDE OF HÖLKENSEIDE G.M.B.H.

guide caused by the motion of the former, by uniting the two thread guides rigidly with one another, so that the second thread guide also takes part in the to and fro motion. In order at the same time to avoid friction of the thread on the guide as far as possible, he provides the latter with small rollers or other revolving bodies, which revolve under the influence of the thread.

A special variety of thread guides are those used in spinning centrifuges. (See below.) In this case the thread must be led vertically downwards and centrically into the rotary spinning-pot and the thread guides have usually the form shown in Fig. 39, and consist of a long funnel-tube, provided with constrictions, through which the thread is passed. The lower end of the tube, from which the thread is withdrawn sideways, is either widened like a funnel or otherwise is provided with a very evenly rounded edge. The constrictions of the tube are for the purpose of damping the oscillations caused by the rapid rotation of the thread produced by the centrifuge, which are transferred to the upper part of the thread. The thread is introduced simply by placing its end on the funnel 2 and pouring water or spinning bath liquid on to it. The liquid

pouring down the funnel tube 1 carries the thread with it. As the vertical outer wall of the spinning-pot has to be covered with the thread, the thread guide is usually arranged to have an up and down motion. Such a thread guide is described by Mancelin in French patent 469,890. A similar thread guide was patented by E. Dubot in British patent 126,263, French patent 497,420 and patent of addition 21,008. This consists of a tube attached to a funnel, the tube being of glass and the funnel of enamelled metal or an enamelled alloy. A contrivance for the purpose of adjusting such thread guides into the correct position was protected by S. Courtauld & Co. and J. Clayton in British patent 104,225, German patent 321,216 and French patent 481,410, but this arrangement should be unnecessary for any reliable and experienced workman. A thread guide of quite another kind for spinning-pots is shown in Fig. 40, and described in German patent 386,532 of the Zellstoffverwertungsgesellschaft and A. Wagner. The arrangement consists of a hollow cone *d*, above which is placed the thread guide *e* with the slot *k*. The thread *b* coming from the guide-pulley *a* runs over the guide *k*, through the cone into the spinning-pot *g*, in which it is wound as a cake b_1 and b_2. The broken line *kih* indicates the thread as it runs up the right-hand side, and the line *klm* as it runs up the left-hand side.

FIG. 39. THREAD GUIDE FOR SPINNING POT

Thread Gutters. In some processes the thread undergoes a further treatment before it is wound. Thus, for example, viscose silk undergoes an after-treatment, whilst cuprammonium silk has to be treated with acid, and so forth. Frequently, these processes are carried out by passing the thread up an upwardly sloping gutter, in which it is met by the acid or other liquid. Fig. 41, for example, shows a contrivance of this kind, as described by A. Wagner in German patent 357,423. The thread *f* passes through the acid *d* flowing in the gutter *a*, on to the winding spool. The acid is discharged through the opening *c* into the gutter from the container *b*; *e* is a weir

over which the acid flows. J. Foltzer proposes the treatment of threads with various liquids in gutters of this kind in German patent 209,923 of 1908. In the arrangement described in Bemberg's German patent 374,507, and shown in Fig. 42, an upper gutter *b*, through which the thread passes is followed by a return gutter *g* sloping in the contrary direction, which passes the acid once more over the silk which is already wound on

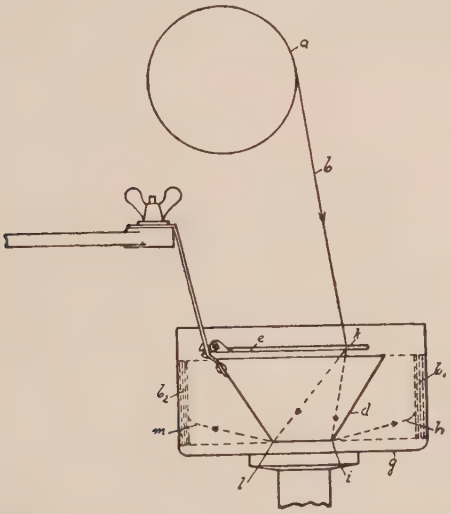


FIG. 40. THREAD GUIDE OF ZELLSTOFFVERWERTUNGSGESELLSCHAFT

the spool *c*. German patent 363,916 of the same firm, deals with the supply of acid to the gutter. A very similar arrangement is described by A. Lauffs, in German patent 362,635, according to which the adjustment of the gutter is effected in such a manner that a considerable portion of the liquid used for treatment runs from it on to the reel which is placed below. The liquid is introduced into the middle of the gutter and flows to both ends, so that during the first portion the thread is washed in counter-flow, whilst in the second portion it runs in the same direction as the liquid. In German patent 345,693, the same inventor describes a special arrangement of the gutter. He embeds the gutters in a supporting beam and joins them

directly to a similarly embedded supply tube for the washing liquid. In order to reduce the very large consumption of liquid usual with thread gutters, M. Hölken replaces the gutter by a container provided with two opposed slots. The thread is passed through both slots, through which a relatively small amount of liquid simultaneously flows. (See German patent 411,333.)

Guide Plates. Formerly, instead of thread gutters, simple guide plates of glass, glazed earthenware, etc., were used, over

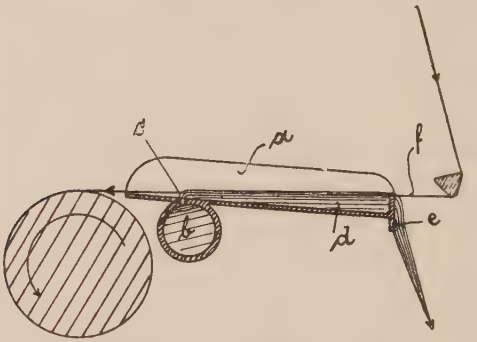


FIG. 41. WAGNER'S THREAD GUTTER

which the thread passed, and on which it could be treated with acids or other liquids. These plates anticipated thread gutters (see, for example, the plates indicated by *g* and *k* in the machine in Fig. 59A). In this machine they also serve the purpose of protecting the thread from damage by the ribs or teeth of the feeding roller should the feed be at any time irregular. According to German patent 391,291, J. C. Hartogs unites the bundles of filament from two neighbouring nozzles by means of a guiding arrangement, and causes them to run on to the bobbin as a single thread. The object of this arrangement is to compensate for the irregularities of the two main nozzles.

Winding Contrivances. According to the manner in which the artificial silk threads are wound, one can distinguish three main types of artificial silk spinning machines, the bobbin or roller machines, reel spinning machines, and centrifugal or

pot spinning machines. In addition, there are machines which spin into stationary spinning pots, which are, however, no longer used.

The most usual form is the bobbin spinning machine, which was at first exclusively used. In this machine, as the name indicates, the thread is simply wound about a revolving cylindrical body—a spool, bobbin, or drum. Reels are now seldom used instead of bobbins, and usually for special materials only. such as artificial horsehair, and so forth. For some years, on the other hand, spinning centrifuges have been much used, in which the thread is led centrally into a rapidly revolving container, the spinning-pot, to the wall of which it is driven by centrifugal force and which it covers in regular windings, forming a hollow cylinder. The bobbin and centrifugal processes each has special advantages and disadvantages, and it is still uncertain whether either possesses any definite advantage over the other.

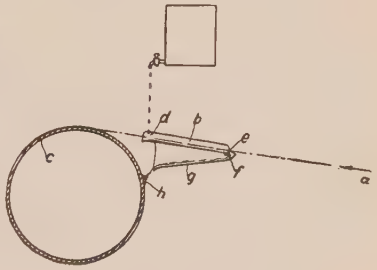


Fig. 42.
Bemberg's Thread Gutter

Bobbin Machines. These were originally the only machines in use. The thread runs on to a rotary cylindrical bobbin. It is wound on to this, and the bobbin both draws the thread from the nozzle and, if necessary, stretches it. (See Figs. 11, 44, 59, and 73.)

Spinning bobbins may be constructed of various materials such as metal, stoneware, glass, celluloid, ebonite, wood veneer (see German patents 379,770 and 396,317), pasteboard, and so forth. Aluminium is the metal which is usually preferred. Aluminium bobbins cannot, of course, be used with an alkaline spinning bath. Metal bobbins are often covered with a coating of varnish, which is always used with cardboard bobbins. The bobbins must not be covered too thickly with the silk, as otherwise this is difficult to wash. On to a bobbin of an average size of about 6 to 20 cm. length and 10 to 12 cm. diameter, 20

or at most 30, grammes of silk are spun, a process which takes from 30 to 40 minutes.

In order to prevent the damage to which cardboard bobbins are liable at comparatively slight pressure, and to avoid metal bobbins, which are unsatisfactory for the threads through the fact that they easily become roughened, F. Küttner constructs bobbins with a metal core covered by varnished cardboard. (See British patent 28,083, 1912, French patent 450,818, Belgian patent 251,191.) In cardboard bobbins the spinning bath, which is usually acid or alkaline, or the washing water, etc., penetrates more particularly from the edge between the layers of cardboard. In order to avoid this action, E. Adolff (French

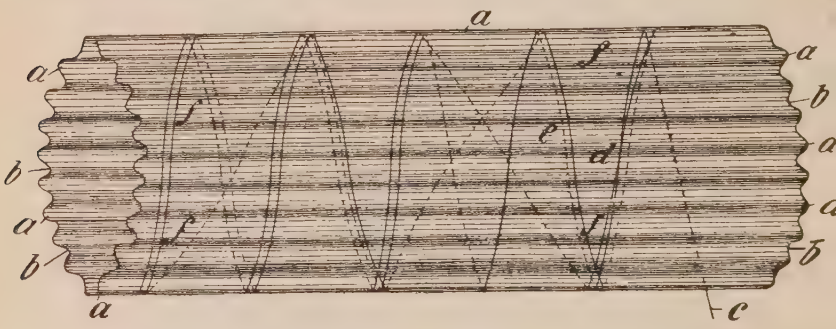
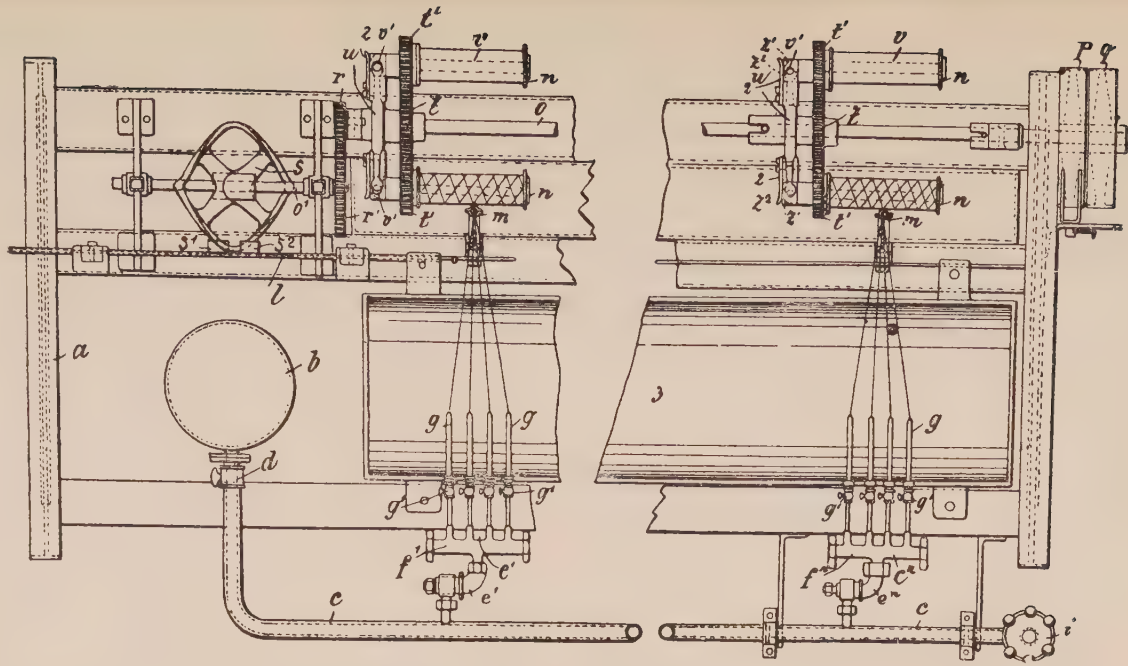


Fig. 43. Corrugated Bobbin

patent 466,210 and Belgian patent 262,989) provides the edges of the bobbins with a ring of resistant material, or he compresses the material of the bobbin more strongly at the edges and polishes the ends. In order to prevent slight deformation of the cardboard bobbins, more particularly through the tension of the silk threads during the drying process, the internal wall of the bobbin is made stronger towards the centre, or it is provided internally with one or more reinforcing rings.

In order to prevent the fracture of glass bobbins, and more particularly to prevent the edges from being chipped—as easily occurs—Röhrens (Austrian patent 27,038, French patent 364,269) constructs the cylindrical portion only of glass, and the lateral portions of metal.

The main portion of the bobbin is, of course, always cylindrical. Occasionally they have at both ends a more or less prominent edge or swelling, which diminishes towards the centre. (See Figs. 45 and 46.) They are not infrequently perforated or provided with grooves in order that the liquid with which the silk is treated on the spools may have even access and be enabled to penetrate the layer of thread. This



(*O. Müller* and *Gebr. Frank*)

FIG. 44. BOBBIN-WINDING MECHANISM

action is also favoured by the cross-winding already mentioned, in consequence of the four-cornered or lozenge-shaped intervals so formed between the individual layers of thread, as is seen, for example, in Figs. 36 (p. 113) and 44. The effect is increased by using cross-winding on perforated or grooved bobbins, or bobbins having longitudinal corrugations, as shown in Fig. 43, which are patented by the Gocher Öelmühle in British patent 4015/1907, German patent 188,910, Austrian patent 32,553, Swiss patent 42,026, and French patent 374,790. These corrugated bobbins have, however, the disadvantage that the threads are more strongly compressed at their points of contact than over the intervals, and consequently, washing and so forth is irregular, and moreover the threads are often marked at the points of contact. O. Müller & Gebr. Franke, in British patent 4078/1911, German patent 257,237, French patent 450,696, and Belgian patent 521,000, endeavour to obtain a specially uniform action during treatment of the bobbins with liquids, by cross-winding the bobbins more thinly at the ends than in the middle, so that the covered bobbins have a barrel-shaped form, and the treating liquid can easily penetrate to every portion of the thread. This condition is attained by moving the thread guide more rapidly at the ends of each bobbin than in the middle by means of a cam disc of special form. The apparatus for this purpose, which is, in general, very instructive, is shown as seen from above, in Fig. 44. The spinning solution is supplied from the container *b* through the supply tube *c*, and the nozzles *g*, to the spinning bath in container 3, from which the threads are carried over the thread-guide *m* to the bobbin *n*. The movement of the thread-guide is effected in the manner already described by the cam disc *s*. With regard to the special arrangement for replacing the bobbins in this machine, see the details on page 126.

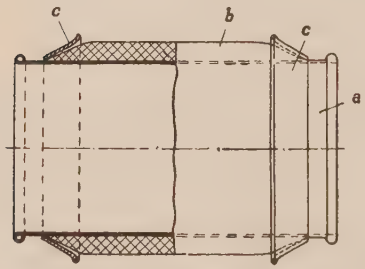


Fig. 45. Kaempf's Bobbin

In order to prevent the thread from being detached or felted

or otherwise damaged by the washing or after-treatment liquids, A. Kaempf, in German patent 414,868, proposes to supply flat, protective rings *c* (e.g. of india-rubber) on the bobbin *a* at both ends of the wound fibre *b*, as shown in Fig. 45.

According to German patent 338,930, Courtaulds, Ltd., provide the bobbins *a* (Fig. 46) with a coating *b*, permeable to liquids, so that the liquid expelled from the innermost layer of wound artificial silk *c* can escape along the bobbin to its ends. F. Küttner, according to German patent 357,137, inserts a lath with notches *a* between the thread-guide *A* and the winding roller *B*, as shown in Fig. 47. These notches cause the thread, which is carried forward by the steadily advancing thread guide *A*, to be intermittently prevented from passing forward, so that intervals occur between the windings, and individual hanks are formed.

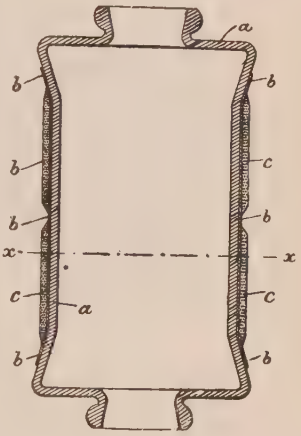


Fig. 46. Courtauld Bobbin

The length and diameter of the bobbins vary greatly. The length, which is usually about double the diameter, varies from about 12 to 50 cm. For special purposes considerably larger rollers are used, such as large winding drums 80 to 100 cm. long and of 50 to 60 cm. diameter. On such drums, which are more particularly used for spinning thicker threads, such as artificial horsehair, the thread from several nozzles is usually wound simultaneously, of course at certain intervals, so that the drum finally carries several (4 to 10) hanks.

In German patent 369,245, K. Schultze and E. Schülke describe a bobbin consisting of a sheet metal cylinder, which is provided with numerous fine perforations (several hundred to several thousand per sq. cm.). According to German patent 324,697, these extremely fine apertures are produced by etching.

In order to expose the artificial silk thread to exceptionally high tension on drying, R. Pawlikowski has designed a special form of bobbin (British patent 16,629/1910, German patents 235,325 and 246,481, and French patent 417,851.) The bars which form the surface of the bobbin rest on elastic rings which are pressed together by

surrounding bands during spinning. After spinning, these bands are loosened, by which means the rods are pressed outwards and the silk is placed under tension. The process is, however, too complicated, and the bobbins too expensive for large-scale production.

Bobbin Drive. The bobbins are usually simply slipped over a special carrier on the central shaft, which turns with the shaft itself. These fittings consist of a sleeve surrounding the shaft, with a cylindrical, polygonal, cross-shaped, or other

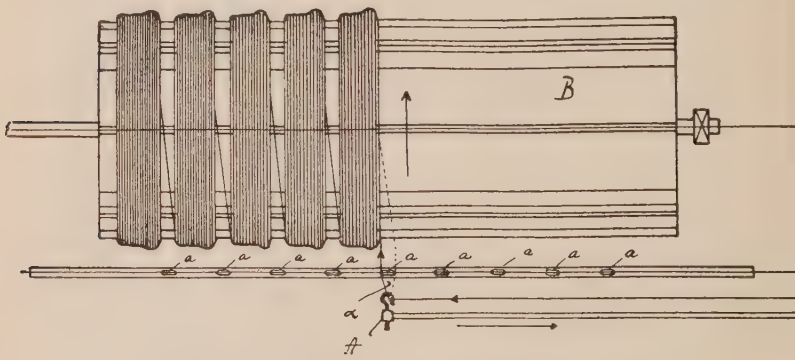
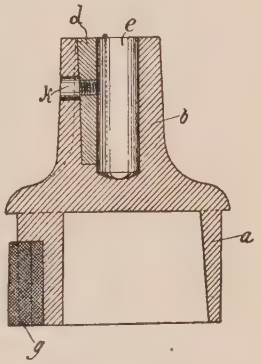


Fig. 47. Küttner's Hank-winding Mechanism

prolongation, which is usually cup-shaped. This is usually constructed of glass, porcelain, or ebonite (wood is not to be recommended) and may be provided with india-rubber strips in order to facilitate the fixing of the bobbin.

Fig. 48 shows such a bobbin carrier in cross-section as described by Metallhütte Bär & Co., in German patent 398,345. The cup-shaped structure *a*, on to which the bobbins are slipped, is constructed in one portion with the sleeve *b*. *g* is a flexible india-rubber band on the circumference of the cup. The arrangement is attached to the shaft by the wedge *d* and the screw *k*. According to German patent 440,965 J. Manquat attaches the bobbins to the carriers by means of resilient wire loops, one arm of which engages with a corresponding depression in the carrier by means of a semi-circular bend. According to French patent 442,593, Burill provides his perforated aluminium bobbins with overfolded ends, with semi-circular depressions raised on the outside, in which balls engage, which are attached by springs or by a resilient ring to the bobbin carriers. A bobbin carrier with special provision for accurately centred rotation is described by A. Kuhn in German patent 381,290.

Spinning machines also exist in which friction pulleys are used instead of the drives already described. The bobbins either revolve freely, whilst supported on the friction pulley, or they revolve on their own shaft and are driven by pulleys which are pressed against them. Such a drive is used, for example, in the spinning machine of Waddel & Petit (British patent 5881/1907, German patent 204,215, U.S. patent 846,879, and French patent 375,633.) The bobbin is also driven by friction from a driving drum in the arrangement described by Lumière in German patent 173,012.



(*Metallhütte Bär & Co.*)

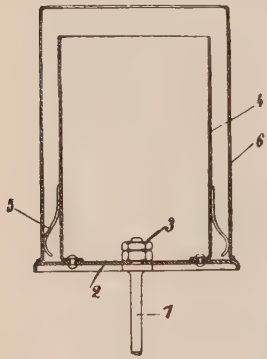
Fig. 48. Bobbin Carrier

In these cases, contact between the bobbins and the friction discs or pulleys usually occurs at the edges of the bobbins only. In German patent 395,953, of the Deutsche Gasglühlicht-Auergesellschaft, and in a similar patent by Küttner and others (German patent 417,941), a machine is described in which the bobbins, or the masses of wound silk thread, lie along the whole length of the shaft. This process might under some circumstances endanger the thread.

Replacement of Bobbins. Formerly the replacement of full by empty bobbins occurred by hand exclusively, and this practice is often followed to-day. A practised workman removes the full bobbin from its fitting, replaces it by a new bobbin, and transfers the thread to the latter. This is all done rapidly, so that the spinning process suffers no interruption. However, deftness and practice are required, for which reason attempts have been made for a long time to render the exchange simpler, or to enable it to be carried out entirely by the machine. More particularly, the winding portion of the machine is now so constructed that a second bobbin lies behind or above each bobbin, usually on its own spindle, and the empty bobbin is made to rotate before the thread is removed from the full bobbin. It is therefore merely necessary for the

workman to transfer the thread, which then continues to be wound by the second bobbin, after which he removes the full bobbin. Sometimes the two bobbins are arranged on a common shaft, which can be turned about an axis lying between them. By turning the shaft through 180° the empty bobbin is transferred to the former position of the full one. (See Fig. 44.)

In the machine described by Soc. Planchon of Lyons, in British patent 13,360/1913, U.S. patent 1,093,146, and French patent 468,809, the interchange of the bobbins is effected automatically at regular intervals by the machine itself by reversing the carrier.



(*A. Pinel*)

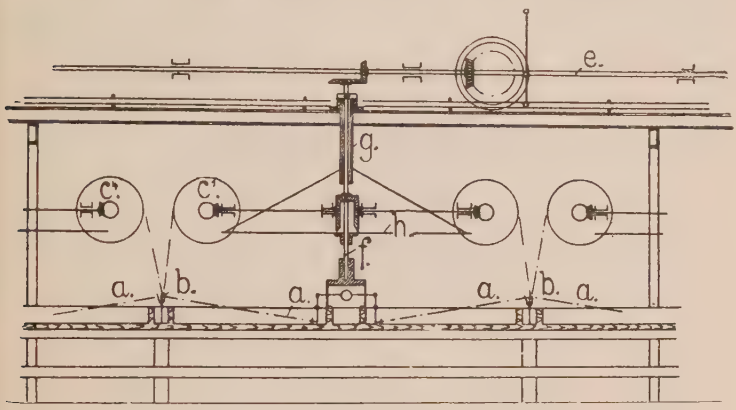
FIG. 49. BOBBIN WITH CONCENTRIC AUXILIARY BOBBIN

The same purpose is achieved in a somewhat different manner in the machine constructed by J. Manquat (British patent 12,710/1912) by automatically releasing the thread from the full bobbin, severing it with a knife, and transferring it to the empty bobbin. A peculiar change of bobbins is described by Lumière in German patent 173,012. In this arrangement, several bobbins are arranged similarly to the chambers of a revolver around a driving pulley, one bobbin at a time being driven by it through friction. When one bobbin is full, another is impelled into the working position.

According to German patent 352,587, A. Pinel provides the spindles which carry the bobbins with a broad rim which forms a small, flat, cylindrical drum, and which is also suitable for winding the thread. When the bobbin is full, the thread is transferred to this rim, and further wound whilst the bobbin is being exchanged. In a similar manner he arranges (as described in German patent 378,231) that within the readily removable spinning bobbin 6 (Fig. 49) a concentric drum 4 is provided, which is firmly attached to the bobbin holder 2 on the shaft 1, on which drum the thread is wound when the bobbin 6 is full and is removed. Both these arrangements suffer from the disadvantage that it is only possible to wind quite short lengths of thread on the supplementary cylinder, thus producing threads of poor quality, which is avoided if the full bobbins are directly replaced by empty ones.

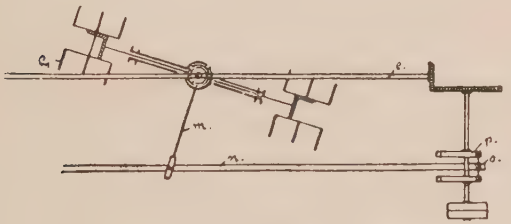
In order to obtain freshly spun thread as a continuous lap, and in addition to ensure uninterrupted spinning, the Köln-Rottweiler Pulverfabriken, in German patent 344,748, claim a spinning and reeling contrivance so arranged that the reel suspended over the spinning bath executes a pendulum motion in a horizontal plane, and each two neighbouring reels are so arranged that the thread from the fully-wound

reel can be transferred to the other. Fig. 50A shows a front view of the machine, whilst Fig. 50B shows the driving mechanism in plan. The thread *a* from the nozzles passes over the thread-guide *b* to the reels c_1 or c_4, which are mounted rotably on the ends of the carrier bar *h*.



(*Köln-Rottweiler Pulverfabriken*)

FIG. 50A. SPINNING AND REELING MECHANISM
Front View



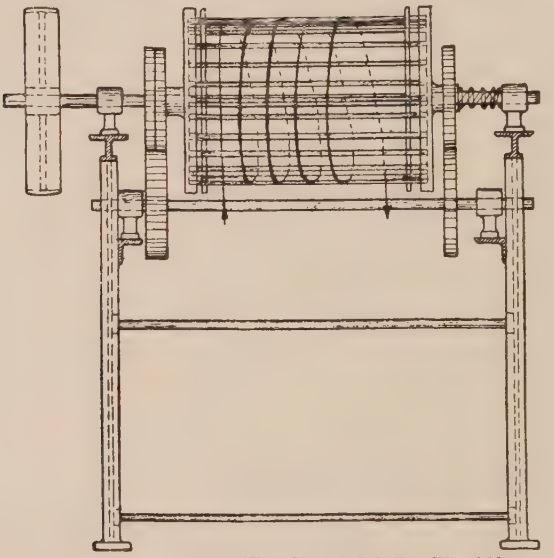
(*Köln-Rottweiler Pulverfabriken*)

FIG. 50B. SPINNING AND REELING MECHANISM
Plan

The rotation of the reel stand is effected by the cam-disc *p* by means of the eccentric rod *o*, the thrust-bar *n*, and the lever *m*.

The winding bobbins usually run with their lower portions immersed in baths which are required for the after-treatment of the thread, for example, for completing the precipitation, fixing, washing, and so forth. Each bobbin is usually provided with its own small bath-box, which just suffices to ensure that the lower portion of the bobbin is immersed in the bath. As

the bobbins are usually at a higher level than the spinning bath containing the nozzles, such a bath is usually called the "upper bath" or "bobbin bath," in contrast to the lower bath, which is the actual spinning or precipitation bath. It is sometimes a disadvantage of this method of working that the inner lengths of thread on the bobbins are less effectively



(*Ver. Glanzstoffabriken Elberfeld*)

Fig. 51. Winding Drum

acted upon by the rinsing bath than the outer layers. A completely uniform action is usually ensured by the treatment of the individual main thread, which is not already part of a thickly wound lap. To carry the thread through a short length of bath will not usually be sufficient. A very long passage through the bath would, however, take up unduly much space and require a very large bath.

This problem was solved by the Vereinigten Glanzstoffabriken Elberfeld, by the winding drum described in German patent 236,548 (French patent 426,089) and additional German patents 239,821 and 239,822. The main length of the thread is carried on to the drum in the form of a helical curve. The surface of the drum is divided into two

groups of segments, which are moved radially to the drum, and parallel with its axis, during which motion they alternately grip the wound thread and pass it on to one another by a lateral displacement. The course of the thread is shown in Fig. 51. The drum can not only be used as a winding contrivance, but also as an intermediate apparatus which carries the thread on to other smaller bobbins. An explanation of this somewhat complicated method of transference would take up too much space ; it may be referred to in the original patent, or, for example, in Süvern, *Künstliche Seide*, 1921, p. 555. (See also Eck's German patent 300,254.)

The treatment of the thread in two baths is also sometimes carried out by providing the spinning frame with two bath containers of about equal size, which are traversed consecutively by the fibre before it is led to the bobbin. (See, for example, Fig. 52.) The two-bath process was formerly much used, but in spite of its many advantages, the one-bath process is now almost universal.

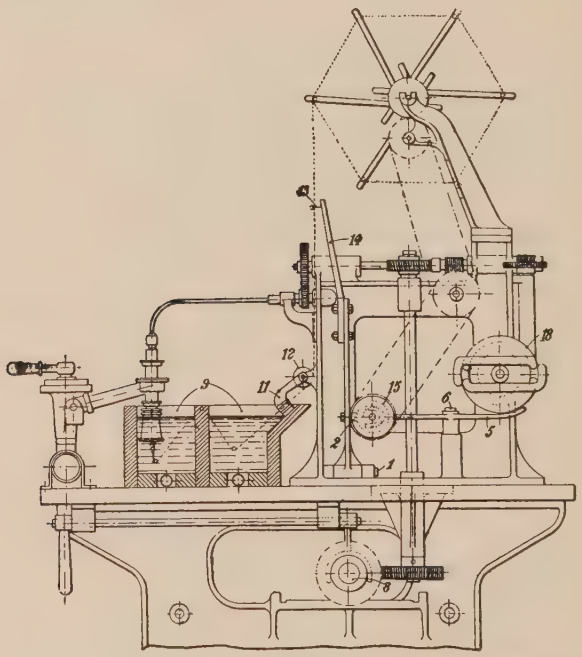
A special carrying frame for the bobbins during joint washing and drying is described in A. Lehner's German patent 363,502.

In the special section we will describe contrivances in which no actual winding of the thread takes place at all, as it is simply deposited in more or less regular spirals in a container. Similarly, according to German patent 345,630 of the Bemberg A.-G., a thread produced without any tension is simply received on a plate movable relatively to the nozzle, in such a manner that the threads are laid together in parallel layers to form a hank. The distance between the receiving plate and the nozzle may be variable. The patent specification describes the contrivance with the help of special drawings.

Reel Spinning Machines. Reels have also been much used as a winding contrivance on spinning machines, and are still used here and there, particularly for threads which do not require to be twisted, such as artificial horsehair, and so forth.

The reels which are used for this purpose are constructed exactly in the same way as those for ordinary reeling machines, and are polygonal, the circumference being formed by laths which are attached to spokes carried by the central shaft. (See, for example, Figs. 52 and 53.) Ordinarily, each nozzle is provided with a narrow reel to take one hank only, or with two, in order to facilitate easy replacement. (See, for example, the arrangement shown in Fig. 52, according to German patent 168,171 of the Société Française de la Viscose.) Long reels of the form of the ordinary hank reel, on which about 10 hanks

may be wound, have also been proposed; for example, the reel shown in Fig. 53, and described in German patent 244,375, in which the threads *c*, discharged by the 10 nozzles *a*, are carried over the oscillating guide bar *b* on to the bars *d* of the reel, which revolves about a shaft *e*. In order to remove the



(*Soc. Française de la Viscose*)

FIG. 52. REELING MACHINE

hanks, the spinning reel and the hank reel are reduced in circumference by displacing one or more bars inwardly. The reels are often so constructed that they are provided with a movable and a non-movable group of bars. An improved reel of this character is described by A. Lauffs in German patent 358,977.

With regard to a locking contrivance for reels for spinning machines, see German patent 368,590, of J. P. Bemberg, A.-G.

Spinning Centrifuges or Spinning Pots. The problem of simultaneously spinning and twisting the fibre, which was discussed in connection with revolving nozzles on pp. 108–110 was solved more or less satisfactorily, as there mentioned, by the use of rotary spinning pots as a winding mechanism. The principle of this process is that the thread, which is spun in the

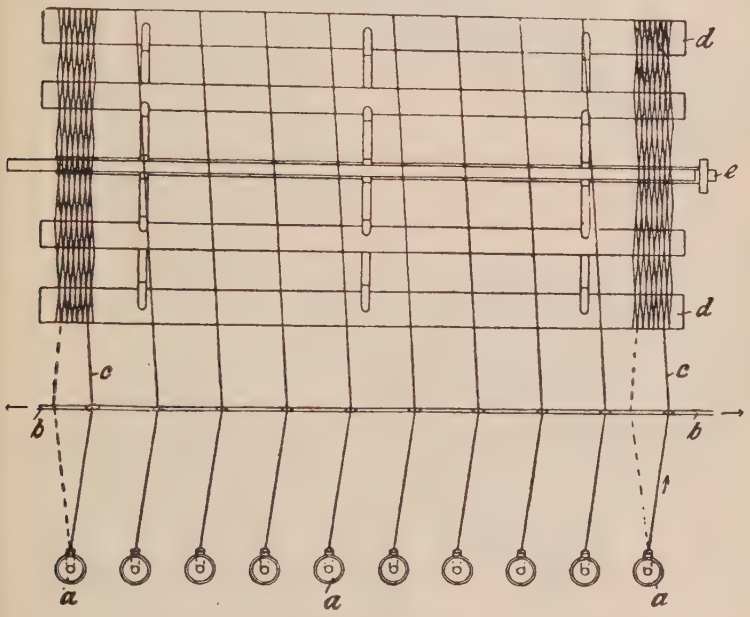


FIG. 53. MULTIPLE WINDING REEL
(German patent 244,375)

ordinary manner, passes through a funnel tube, which serves as a thread guide, into a rapidly revolving pot. Centrifugal force flings the thread to the wall of the pot as soon as it comes into contact with its floor, and the same action maintains it in contact with the wall and carries it along, so that a pull is exerted on the thread, which assists its further discharge from the nozzle.

As the thread is in this manner diverted from the direction in which it was introduced at an angle of about 90°, it is turned about itself and thus twisted.

The first pot-spinning machine was due to Chas. F. Topham, and is described in British patents 23,157/1900, and 23,158/1900, German patent 125,947 (1900), Austrian patent 9,548, and German patent 127,064, Swiss patent 24,301, and U.S. patent 702,382. It is shown in Fig. 54. The thread issuing from the nozzle is carried over the guide pulley k, through the funnel l, into the spinning pot m, which is mounted on the axle n and revolved by the driving pulley n^3. The spinning pot

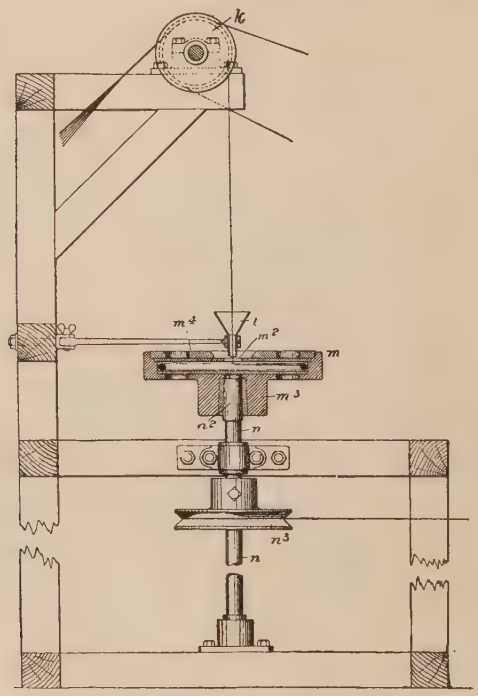


Fig. 54. Topham's Pot-spinning Machine

is quite shallow, and the rate of revolution would now be considered very small.

R. Linkmeyer suggested the use of a rotary spinning pot, more particularly for cuprammonium silk, to which—apart from the rotary motion—an oscillating motion was imparted, so that the threads in the spinning pot were deposited in intersecting layers. (British patent 6,356/1905, German patent 169,906, Austrian patent 28,595, Swiss patent 35,434, and French patent 352,528.) J. M. de Sauverzac described a similar spinning pot in French patent 420,085, in which the thread is deposited spirally.

These machines may be contrasted with a modern machine

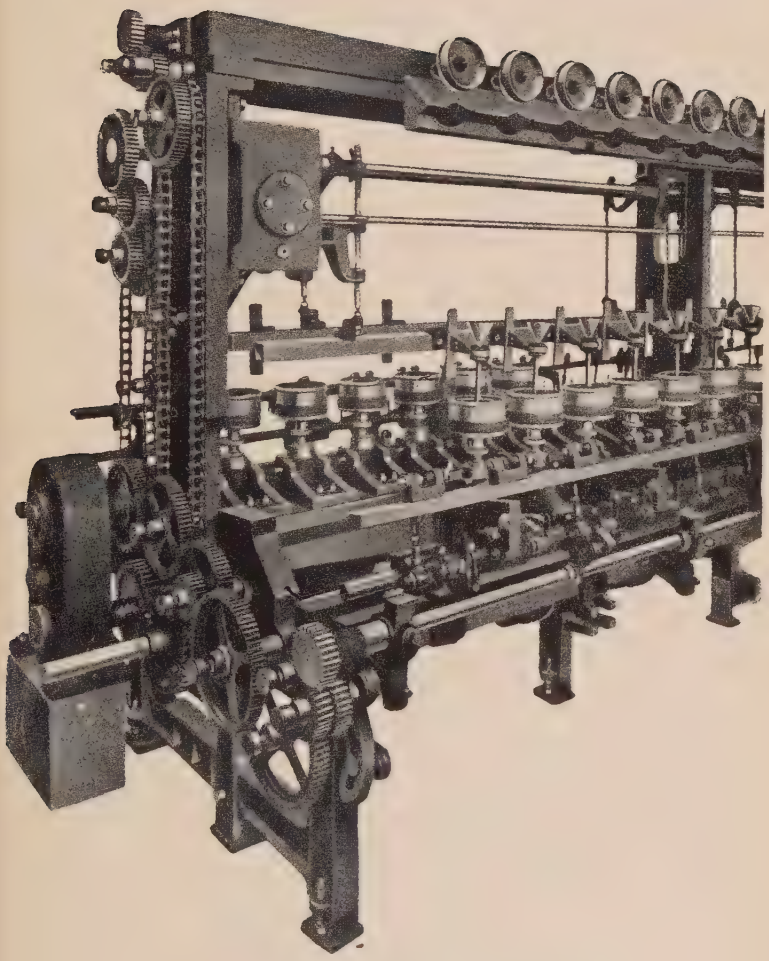


FIG. 55. POT-SPINNING MACHINE

of this type, which is shown in Fig. 55. It will be seen from this figure that the path followed by the fibre from the nozzle to the winding mechanism (the spinning pot) is much longer than in bobbin machines, and the distance from nozzle to guide pulley is about one metre. Machines are also constructed in which this distance is less than one-half, but in that case the spinning pots must lie at a lower level than the nozzle, as it is found by experience that the distance between the guide pulley and the spinning pot—especially for fine qualities—must be between 80 and 90 cm., as a certain weight of thread, which is of course dependent on its length, is necessary in order to prevent the thread from winding round the guide pulley.

The thread guides used in this case have already been described in our description of thread guides in general (see page 113 *et seq.*).

The size of spinning pots varies ; some are about 15 to 21 cm. in diameter and 7 to 10 cm. high. A diameter of 16 cm. is very usual. The pots are always constructed of cast or spun aluminium, and are covered internally with acid-proof varnish. Linings of glass, or more frequently of ebonite, are often used. Several openings are provided in the wall through which the precipitating liquid carried in with the thread can escape by centrifugal action. The rate of revolution of spinning pots is on the average 4000 r.p.m.

The drive of spinning pots initially caused many difficulties, and all possible forms were tried : gearwheel and helical drive ; electric drive, with small three-phase motors ; belt drive ; friction drive ; electro-magnetic drive, in which a steel band is pressed by an electro-magnet on to a disc on the shaft of the centrifuge, and carries this round, similarly to the manner in which the spindles of doubling machines are carried round by a belt ; and, finally, water-turbine drive.

The electro-magnetic drive and the drive by friction discs have proved the least satisfactory. The direct drive by electric motor on the centrifuge shaft (shown in Fig. 56 and described in German patent 370,398), which offers the advantage of a

perfectly uniform rate of revolution, is comparatively expensive. In Fig. 56, the thread 1 passes over the guide pulley 2, through the thread guide 3, to the spinning pot 4; and a common shaft 6, driven by the motor 7, passes through the bearing 8, which is supported by the table 5. The helical drive is also somewhat dear, and has the disadvantage that the wheels wear very rapidly at high rates of revolution. In spite of many disadvantages, transmission by small belts has been found relatively satisfactory, as has also turbine drive with high pressure water. (Regarding the latter, see, for example, German patents 363,300 and 413,158 of C. G. Haubold, Chemnitz.) A centrifugal spinning machine of the latter kind, with high pressure hydraulic drives, and built by this firm, is shown in Figs. 57A and 57B, in longitudinal and transverse section. A spinning-pot drive with especially elaborate protection of the bearings, and so forth, against dust, is described in Bezold & Glafey's German patent 354,513.

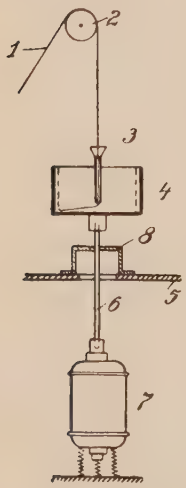
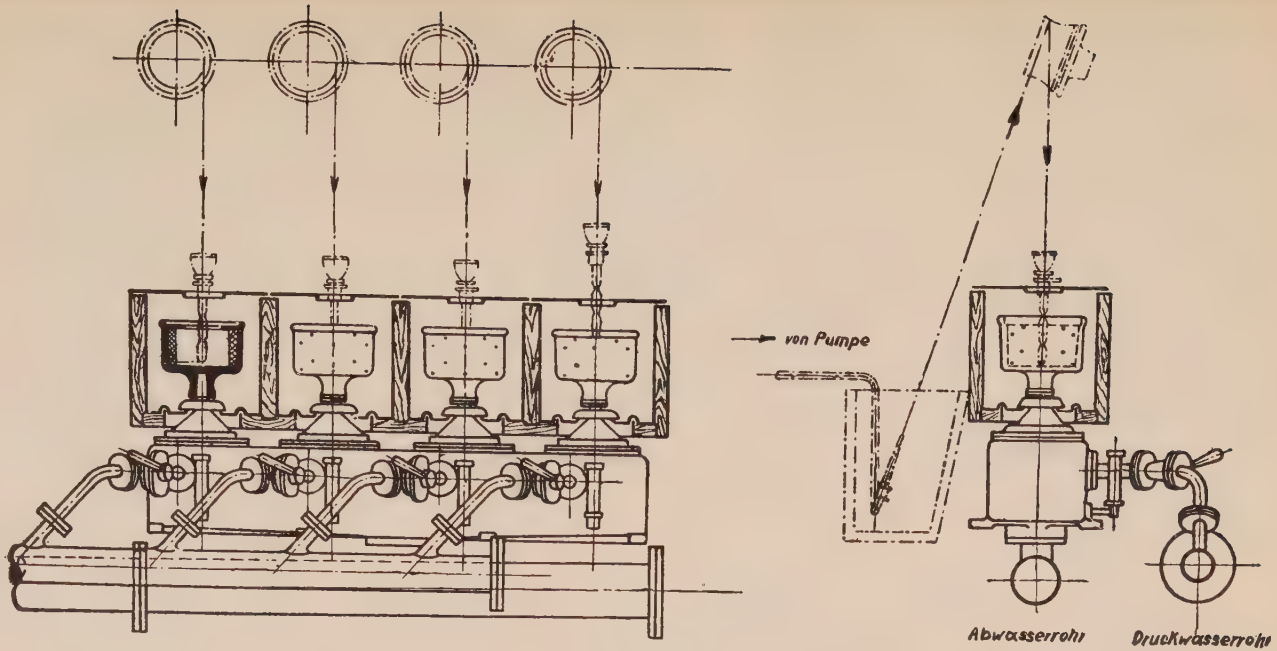


FIG. 56. SPINNING POT WITH ELECTRIC DRIVE

The spinning pots must be very exactly balanced, so that they may run centrically. In British patent 139,104, an arrangement is protected by which exact adjustment is achieved by suitable mounting of the driving motor on three elastic buffer-like bearings. A well-centred adjustment may also be achieved by a suitably arranged ring of mercury or by a steel ring, the centre of gravity of which can be displaced as required. In German patent 409,962, N. V. Nederlandsche Kunstzijdefabriek, Arnhem, endeavours to avoid the occurrence of vibrations or strain, and therefore of whipping, by driving the spinning pot by two friction discs instead of by one, as is usual, and in such a manner that the two friction discs bear symmetrically on the shaft of the gearwheel at both sides of the casing of the centrifuge. An attempt to solve the same problem is made in German patent 370,398 of Siemens-Schuckert-Werke, in the following manner: The shaft which



FIGS. 57A AND 57B. POT-SPINNING MACHINE

(*C. G. Haubold, Chemnitz*)

von Pumpe denotes "from pump"
Abwasserrohr denotes "waste water pipe"
Druckwasserrohr denotes "high pressure water pipe"

connects the motor directly with the spinning pot takes the form of a flexible bar, which is so thin that during its revolution the spinning pot adjusts itself along its axial centre of inertia, independently of the motor, without the production of serious pressure on the bearings (see Fig. 56). The same firm attempt to solve the problem in another manner in their German patent 363,301, by arranging the point of discharge of the thread as the centre-point for the vibrations which occur during rotation.

The mass of thread forms an annular cake in the spinning pot, which is removed by inverting the pot. In order to avoid the assumption by the cake of a domed or sharp rim, the spinning pot is sometimes provided with a lid.

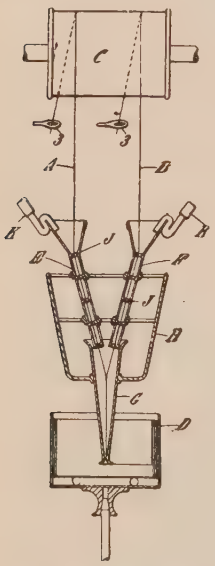


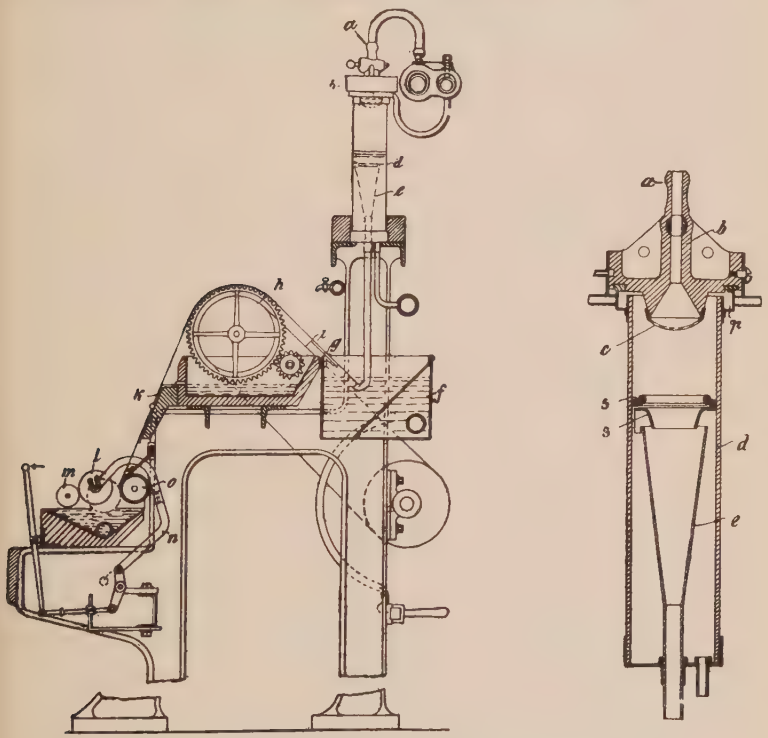
Fig. 58. Dreaper's Doubling Spinning Pot

According to German patent 350,327, R. Bader places a ring-shaped spring inside the thread in the spinning pot. The diameter of this ring can be reduced, and it forms a support for the cake during reeling, thus avoiding any tangling of the thread.

Spinning pots may be used, not only for twisting the main thread, but also for doubling several main threads. In German patent 373,795, Dreaper describes a contrivance for this purpose, which is shown in Fig. 58. The threads *A* and *B*, passing from the guide-pulley *C*, first run separately through the guide tubes *E* and *F*, and unite in tube *G*, in which they are doubled on one another and finally wound in *D*. As the twists of the revolving thread are transferred into the tubes *E* and *F*, each thread is first twisted alone in each of these tubes. *J* represents ribs within these tubes in order to reduce the friction of the threads on the walls. *K* are conduits for the water or precipitation bath, serving for the introduction of the thread.

An interesting contrivance is patented by H. Jentgen in German patent 368,567, consisting of a combination of a bobbin spinning machine and a pot-spinning machine, in which either process can be carried out at will, which is often desirable when spinning threads of various thicknesses. For example, the winding spool may be used as a guide pulley only, or a removable winding spool may be used in place of a guide pulley, or removable spinning bobbins may be specially arranged between the guide pulley and the spinning pot.

The twisting which the artificial silk thread undergoes in the spinning-pot process is not sufficient for all purposes, particularly as spinning is usually conducted at a considerable speed, such as 80 metres per minute. At this velocity, 4000 revs. per min. would only produce 50 twists per metre. Naturally, a higher degree of twist can be obtained at a lower spinning



FIGS. 59A AND 59B. BEMBERG'S STRETCH-SPINNING MACHINE

speed, but usually, especially for warp threads, this only amounts to a preliminary twist. In this case, therefore, as compared with the bobbin spinning process, one does not save rewinding and twisting operations, but only the former.

In general, it may be said that the bobbin process is simpler and easier to carry out, and the necessary machinery less complicated than for the pot-spinning process, but that the

latter enables a larger output per unit to be achieved, and for this reason and by saving re-winding, it is more economical. The higher initial cost of the machine is compensated by the extraordinarily large consumption of bobbins in the bobbin spinning process.

The spinning frame described by Denis and the Obourg Artificial Silk Works, in German patent 287,968, and Belgian patent 263,133, is very original. In order to accommodate as many nozzles as possible per metre of the machine, and to arrange each nozzle so that it may be readily accessible to the operator, they are arranged in a closed circle with a rotary nozzle carrier. This arrangement is, however, seldom used technically.

The Stretch-spinning Process. The process of discharging the silk from the nozzles in the form of a relatively thick thread which is then stretched to a very fine thread by a rapid pull, was first applied by F. Lehner in the case of collodium silk. (See German patent 58,508, and Swiss patent 3740.) E. Thiele transferred the process to cuprammonium silk, and developed it further. He used a slowly-acting precipitating liquid, or two precipitating liquids—one of which floated on the other—so that the thread was first exposed to the slowly acting liquid during the stretch process and then passed through the energetically-acting decomposing liquid. (See British patent, 8083/1902, German patents 154,507 and 157,157, French patent 320,446, Austrian patent 21,119, U.S. patent 710,819, and also German patent 173,628, and Austrian patent 27,671.) The stretch-spinning process was later adopted for other silks; for example, for viscose silk (Elberfelder Glanzstoffabriken), and acetate silk (Bayer-Leverkusen). We will describe these processes further in a special section.

The conveyance and stretching of the fibre by a rapidly-moving precipitation bath was more particularly adopted by the firm of J. P. Bemberg for cuprammonium silk, in their stretch-spinning process. Figs. 59A and 59B show the installation necessary for this purpose, as described in British patents 8711, 15,448 and 15,449 of 1908; German patent 220,051, Austrian patent 45,320, Swiss patents 44,507, and 44,963, U.S. patent 957,460, and French patent 390,178.

The spinning solution passes through the tube *a* to the

multiple nozzle *c*, which is carried in the nozzle head *b* ; from this nozzle the bundle of threads passes through the glass cylinder *d*, containing the precipitation bath, and through the glass funnel *e*, which passes through the floor of the cylinder into the container *f*, which contains the spinning bath. From here the thread passes over the guide-plate *g*, and the toothed conveying wheel *h*, to the winding contrivance *lmno*. The arrangement of the precipitation cylinder is shown in Fig. 59B. The fresh precipitation bath enters through a lateral supply pipe into the hollow ring *p*, and over the inner rim of the same into the precipitation cylinder, from which it passes further through the glass funnel *e* into the receiver *f*. From this it is carried by a pump through a pressure regulator and back into the precipitation cylinder through a tube passing through the base of the latter. It rises in this cylinder and flows down over the edge of the glass funnel *e*. The double ring *s* above the glass cylinder, which is made tight with a rubber ring, prevents eddies from being formed in the precipitation liquid above the funnel, and also prevents the fresh precipitation liquid from being carried down too rapidly by the circulating bath. The toothed feeding wheel *h* with the small counter-wheel *i*, serves the purpose of breaking any wave of liquid which may be formed through the too rapid revolution of the pulley, and which might otherwise damage the thread. The gradual reduction in width of the channel for the liquid, caused by the shape of the funnel, causes the rate of flow of the precipitation bath to increase steadily in a downward direction. The thread is therefore at first surrounded by a slowly flowing liquid, and is only carried away by the more rapid stream after it has been partially stretched and partially hardened in the more slowly-moving upper bath, and has therefore become more resistant, after which it is caught up by the more rapid current and more or less stretched during its further process. According to the strength of the precipitation bath and the velocity of the same, the coagulation, hardening and stretching of the fibre can be varied within wide limits. The machine is therefore suitable both for the ordinary spinning process with immediate hardening of the thread, or for the stretch-spinning process.

In the arrangement patented in German patent 413,790, which is otherwise similar, the precipitation liquid is introduced laterally near the lower end of the funnel tube and passes partly upwards and partly downwards, so that the thread descending from above is first treated in counter-current, and only treated by the current flowing in the same direction after it has been hardened to a sufficient extent. In another very similar spinning contrivance, patented by the Cuprum A.-G., Glarus, in German patent 408,447, the precipitating liquid is introduced through an annular channel below the rim of the conical funnel, in order to ensure a uniform overflow of the liquid into the funnel. Arrangements for cleaning spinning apparatus of this type are described in German patents 408,889 and 413,791.

CHAPTER VIIIA

FINISHING ARTIFICIAL SILK

For converting the spun artificial silk into a marketable commodity the following processes are required: washing, drying, doubling, reeling, bleaching and dyeing; apart from special after-treatment for the purpose of water-proofing, softening, dressing, and so forth. Additional treatments are required according to the method of manufacture, such as denitration in the case of collodium silk, the removal of copper from cuprammonium silk, the removal of sulphur from viscose silk, and so forth. These special after-treatment processes will be described in a special section under the heading of the various individual processes.

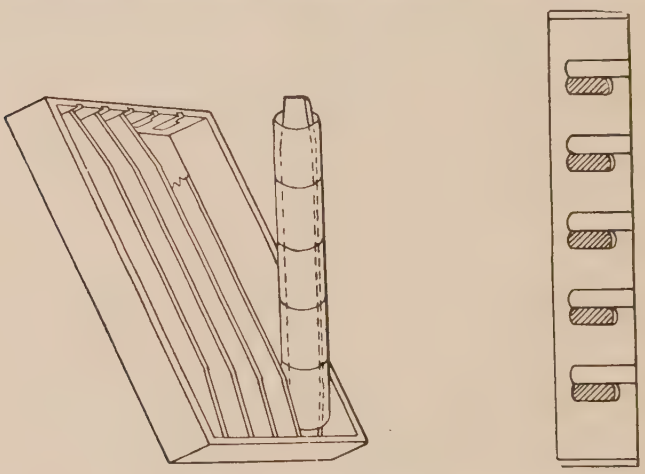
The dyeing of artificial silk will also be treated in a special section, page 39 *et seq.*, as this process occupies a special position among the finishing processes on account of its importance and the variety of methods of carrying it out. Moreover, dyeing is not usually carried out at the artificial silk works, but in special dye-works. For similar reasons, finishing, and so forth, will be discussed in connection with the treatment and applications of artificial silk.

Washing the Silk. The first washing of silk obtained on bobbins almost always occurs on the spinning bobbins as they come from the spinning machine. It is only in the so-called continuous process and similar processes that the thread is wound on to the bobbin in a completely washed condition, and can therefore be further treated without further washing. The washing of the bobbins occurs either in large tanks through which the washing water flows, or on special washing frames.

According to German patent 187,090 of Fürst Guido Donnersmarck-schen Kunstseide- und Acetatwerke, the washing vats containing the bobbins are arranged adjacent to, or over one another in batteries, and the bobbins are systematically washed on the counter-current principle. The arrangements and methods of working described in the patent specification for superposed batteries of washing vats offer

no advantage compared with less elaborate processes. Systematic extraction in adjacent vats, on the other hand, is frequently used. The washing frame described by F. Küttner in German patent 271,656 is very practical, both for transport and for direct insertion into the washing vats. As shown in Figs. 60A and 60B, the bobbins are placed over laths which are held tightly in the grooves of the transverse laths of the frame after slight lateral displacement. The bobbins and the silk on the same are protected from damage to an exceptional extent by this arrangement.

Washing on the counter-current principle is also effected by a very simple and convenient process which Fremery and Urban patented in British patent 6641/1899, German patent 111,409, Swiss patent

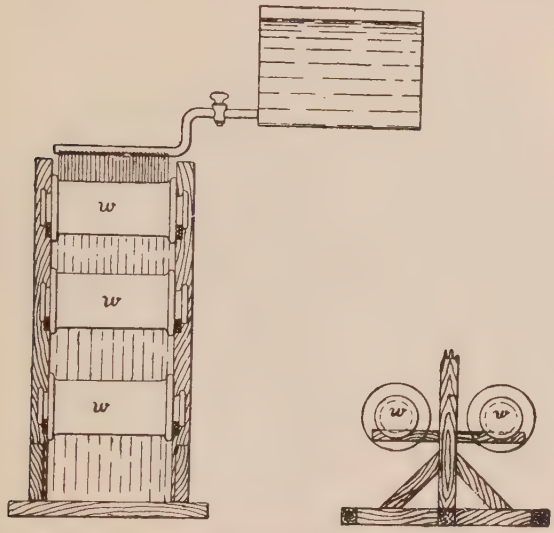


FIGS. 60A AND 60B. KÜTTNER'S BOBBIN WASHING FRAME

19,062, Austrian 6843, and U.S. patent 661,214. The large glass bobbins *w*, wound with the silk (Figs. 61A and 61B), are carried above one another on the arms of wooden stands. The fresh washing water pours on to the upper bobbin and so to the second, third, and so forth, so that the lowest bobbin is treated with the water which is most highly contaminated with salts and other impurities. A washing action on this bobbin occurs, however, as it is the least thoroughly washed. When the uppermost bobbin has been completely washed, each bobbin is raised one stage, and a further unwashed bobbin is placed at the bottom. The washing effect is produced with comparatively small quantities of liquid, as would be expected from a process such as this worked on the counter-current principle. (See also the similar process of Herminghaus, described in German patent 391,290.)

The washing machine described by J. Foltzer, in German patent 165,577, and French patent 353,973, is very similar in principle, but much more complicated. According to this patent, the bobbins—

which are similarly placed above one another on a stand—are automatically sprinkled, moved, and simultaneously turned. The washing machine described by E. Mertz in Swiss patent 34,854, and French patent 364,913, is of similar construction. During the movement of the bobbins, their protruding rims revolve over lateral bars, so that the bobbins are rotated by friction. Another useful process, but which works no better than, for example, the above described Elberfeld washing process, is that described by E. W. Friedrich in British patent 12,842/1906, German patent 178,410, Austrian patent 31,802, and



FIGS. 61A AND 61B. FREMERY AND URBAN'S BOBBIN WASHING FRAME

French patent 366,793, according to which the bobbins, which slowly revolve in the washing liquid, only dip into the same to the extent of about one-half, so that the liquid is uniformly distributed throughout the whole body of the thread, and easily penetrates into the deeper layers of the same. Another contrivance for washing artificial silk on the bobbins is that designed by Pinel, and described in German patent 399,311. It is shown in Fig. 62. The bobbins 5 are attached to the circumference of a wheel 3, which is rotated by two drives ; one for slow revolution whilst washing and another for rapid revolution when centrifuging. One portion of the circumference of the wheel is surrounded by a spraying supply 7, whilst the whole circumference is surrounded by a casing which catches the centrifuged liquid.

Drying. Before re-winding, the washed silk is usually more or less completely dried on the spinning bobbins, as it can be less satisfactorily treated further in a moist condition on

account of its decreased strength. If necessary, it can be re-wound while still damp, but it is almost impossible to double it in this condition, as this process makes greater demands on the thread. The thread must therefore be dried either before or after re-winding. The drying process is carried out in capacious drying chambers heated by steam. Fig. 63 shows a

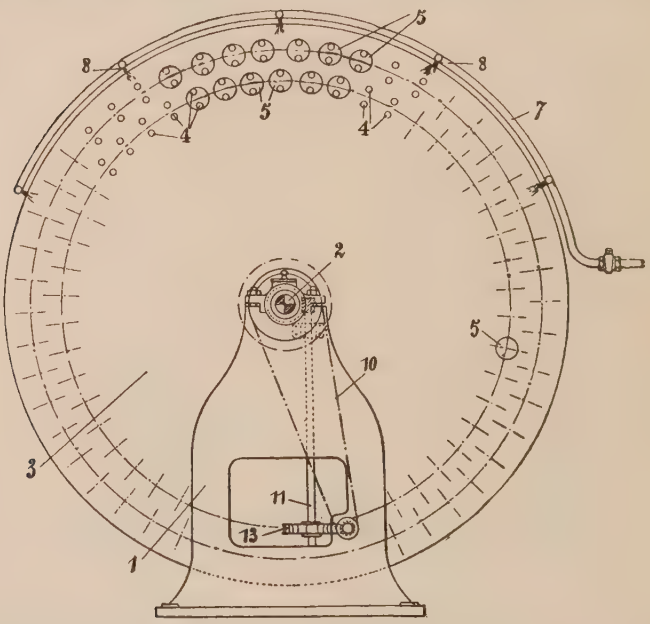


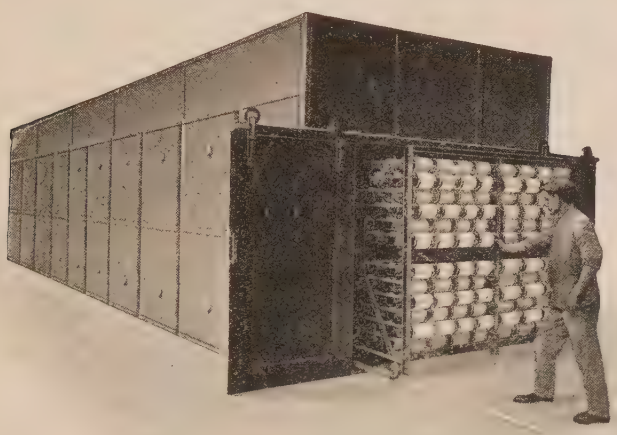
Fig. 62. Pinel's Bobbin Washing Frame

drying chamber specially built for drying bobbins of artificia silk, by the firm Friedrich Haas, Lennep, Rheinland.

The silk must not be dried too far, but as in the case of al textile materials, the fibre should retain a certain amount o moisture (about 8 to 10 per cent, according to its hygroscopi qualities) as it then possesses a greater elasticity and is muc more easily worked than if it were thoroughly dry. For thi reason arrangements must be made to maintain the necessar atmospheric moisture in the following manufacturing processes This is effected by suitable humidifying plants, which pass

fine water spray through the air at various points on the premises, so that it may always be saturated with water vapour. This is a precaution of considerable importance, which is also used for other textile fibres, such as cotton, linen, or silk, and is therefore well known to all those engaged in textile manufactures.

It is the usual practice to spin on to large bobbins and to re-wind these on to smaller bobbins, which are usually of solid



(*F. Haas, Lennep, Rheinland*)

FIG. 63. TUNNEL DRIER FOR BOBBINS

wood, from which latter the fibre is easily doubled. The fibre is usually spun on to large bobbins, as these run more smoothly than small ones and it is not necessary to revolve them so rapidly. The thread is therefore wound more smoothly and evenly. On the other hand, it is not easy to double the fibre directly from large bobbins, as on doubling, the bobbin carrying the thread has to be revolved very rapidly, and large bobbins are unsuitable for this purpose. Also, the " balloon " which the thread forms on doubling would be very large, so that more frequent breakages of the thread would occur through the greater centrifugal action.

The re-winding process is shown in Fig. 64. The thread *d* runs from the stationary spinning bobbin *a*, through the thread guide *b*, on to the small revolving bobbin *c*. From this

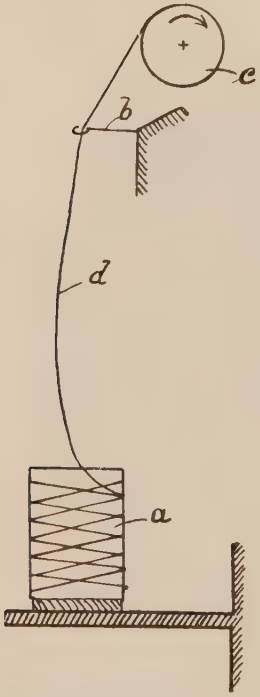


Fig. 64. Diagram of Re-winding Mechanism

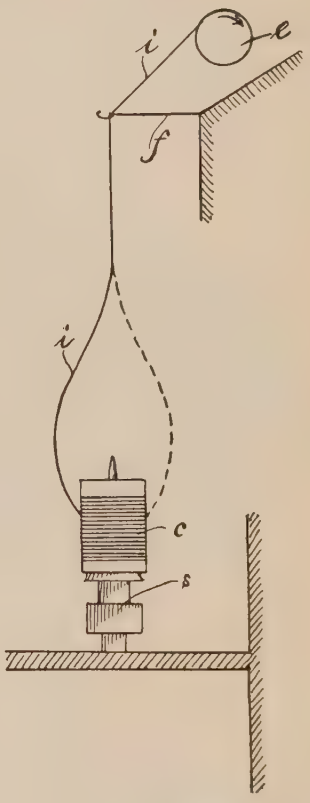
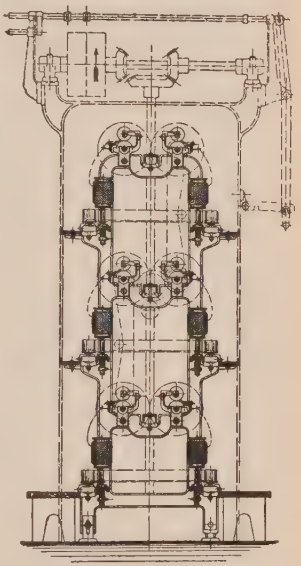


Fig. 65. Diagram of Twisting Mechanism

figure the very simple construction of a winding frame can readily be understood.

Occasionally the threads are converted direct from the spinning bobbins into the form of hanks without strong doubling, more particularly for qualities which are to be sold as so-called "trama vaga," or loosely twisted tram thread. German patent 218,586, for example, describes a machine for

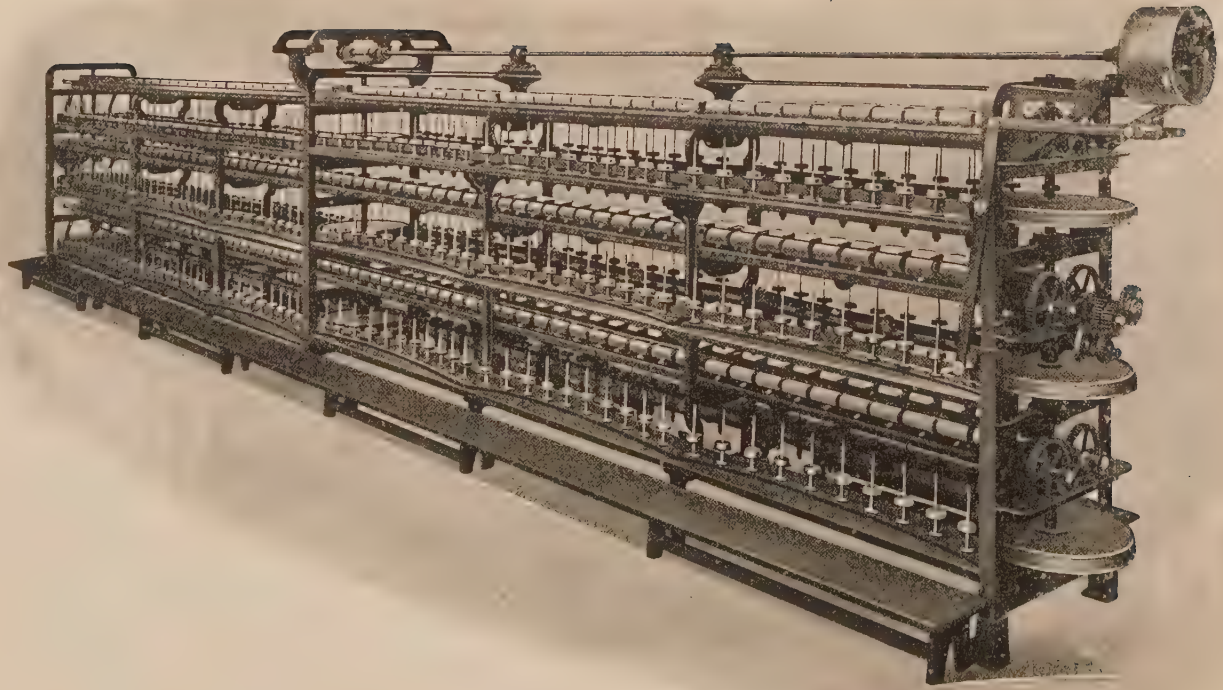
the direct reeling of spinning bobbins on to hank reels. In this machine the thread guide is vertically adjustable. The threads are allowed to swing so far from the bobbin under the influence of centrifugal force that they do not touch the upper rim of the bobbin. In order not to damage the thread through friction on the glass edges when unwinding from glass bobbins, E. Fougeirol, in French patent 337,693, employs a rotary axis within the glass bobbin, the upper end of which is provided with a cap which overlaps the edges of the bobbin, and is constructed, for example, of polished zinc.



(*Oscar Kohorn & Co., Chemnitz*)

Fig. 66.
Multiple Twisting Machine

Doubling. If the thread is re-wound when damp, it is first dried, and after drying—or otherwise immediately after re-winding—it is doubled. Through the doubling process the thread receives a twist, i.e. the individual fibres are twisted round one another. The twist is expressed by the number of turns per metre. Doubling is usually carried out on the well-known multiple-stage doubling frames used in the cotton industry. The diagrammatic figure 65 explains the doubling process quite simply. The small bobbin *c*, on to which the silk has been re-wound, is attached to the rapidly rotating spindle *s* by means of which it is itself rapidly rotated. The thread *i*, which is longitudinally withdrawn from the bobbin, forms a " balloon " under the action of centrifugal force, and is twisted, whilst the bobbin *e*, which is also rotated but with lower velocity, simultaneously withdraws the thread and winds it. *f* is the thread guide. It is quite obvious that the number of twists imparted to the thread per metre depends on the ratio of the rate of revolution of the two bobbins *c* and *e*. If, for



(Oscar Kohorn & Co., Chemnitz)

example, c revolves 60 times whilst e withdraws one metre of thread, the thread receives 60 twists per metre. Fig. 66 shows a diagrammatic cross-section, and Fig. 67 the actual appearance of a three-stage doubling machine, constructed by Oscar Kohorn & Co., of Chemnitz and Vienna. As we have already seen, the thread produced on the centrifugal spinning frame is

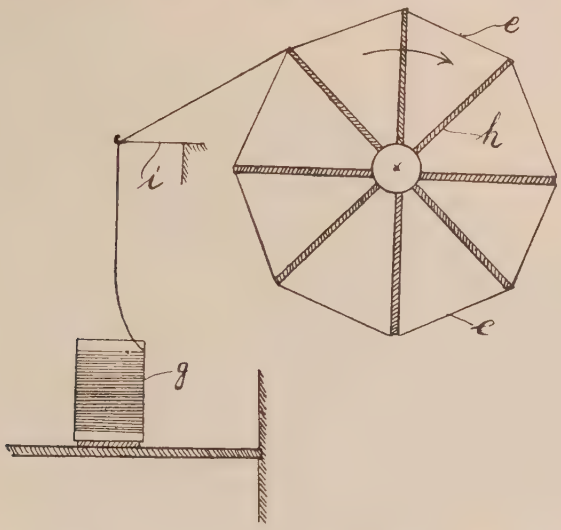


Fig. 68. Diagram of Reeling Mechanism

already considerably twisted. For some purposes this twist is sufficient, whilst for others it must be further increased.

A peculiar method of operation and guidance of the thread is described in German patent 388,365, and additional patent 388,946, by Kaufmann and Sinkwitz. According to these patents, the doubled thread is carried by flowing water through a sinuous conduit, at the outer edge of which it is taken up by a revolving reel. The process is complicated, and does not appear to offer any practical advantages.

Reeling. Usually the thread is required in the form of hanks, not only for sale but also for certain courses of further treatment, such as bleaching and dyeing. This form is imparted to the thread by reeling. This process, and the machines employed for the purpose, are not essentially different from those used for the same purpose in the cotton industry. Fig. 68

gives a diagrammatic representation of the reeling process. The twisted thread on the bobbin *g* is withdrawn by the revolving reel *h*, through the thread guide *i*, and reeled as a large circular hank *e*. The reel usually has a diameter of about 40 to 50 cm. and a length of 100 to 120 cm. 8 to 10 hanks can be simultaneously reeled in parallel. The thread guides are attached to a bar which oscillates during the revolution of the reel, carrying out a stroke of the width of a hank, namely, about 5 to 6 cm. In consequence, cross-winding is produced, which is very shallow in consequence of the rapid revolution of the reel. The reel is provided with a contrivance by means of which its circumference can be greatly reduced by folding inwards some of the bars (usually one or two) which form its circumference, in order that the hanks may readily be removed. Before their removal the hanks are skeined ; that is, they are tied together at three or four places by threads which hold together definite bundles of thread at the points in question, and thus prevent them from becoming tangled. In addition, each reeling frame is provided with a counter which records the number of revolutions, and therefore the length of the thread which has been wound. The ordinary length of thread in a hank is 900 metres. The counter is usually provided with an arrangement which ensures that the reel shall stop automatically after receiving the required length of thread.

Should a thread break during reeling, the operator must immediately stop the machine until it has been re-tied, as otherwise the hank in question would contain too little thread, and moreover would show too low a denier number on weighing (see page 160).

Fig. 69 shows a diagrammatic cross-section of a reel frame constructed by Oscar Kohorn of Chemnitz and Vienna, which is depicted in Fig. 70.

An attempt was made by Count A. Luxburg to combine the operations of re-winding, doubling, and reeling in a single process. This process is described in British patent 1407/1909, German patent 212,954, Swiss patent 47,395, and French patent 398,424, of the Fürst Guido Donnersmarckschen Kunstseiden- und Acetatwerke. The thread is carried directly from the rapidly revolving spinning bobbin *a* (Fig. 71) over the thread guide *b*, on to the reel *c*. Practical experience did not

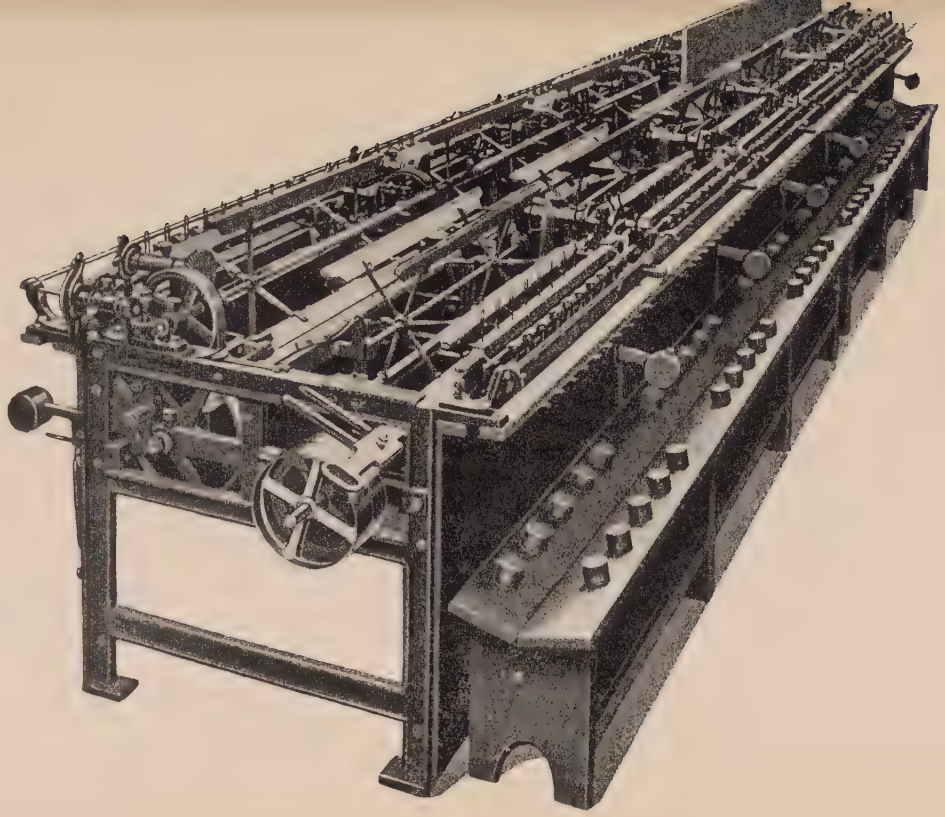
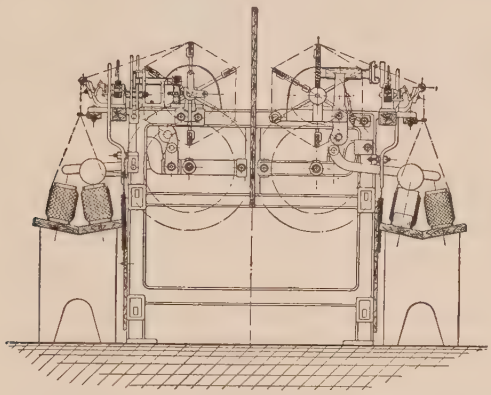


FIG. 70. REELING MACHINE

confirm theoretical expectations, and the process proved impossible in practice. The same remarks apply to the very similar process described in British patent 1022/1911, by Fox and Myers, which is very similar but is further complicated by the intermediate treatment of the thread with a liquid; and also the process patented by R. Pawlikowski in German patent 237,200, according to which the wet, pre-treated yarn on the spinning bobbin is doubled, dried on a drum, and wound or reeled in one process, during which the correct course



(Oscar Kohorn & Co., Chemnitz)

FIG. 69. REELING MACHINE

of the thread is to be ensured by cleaning rollers subsequent to the supply and withdrawal rollers.

On the use of reels in spinning machines, see page 129 *et seq.*

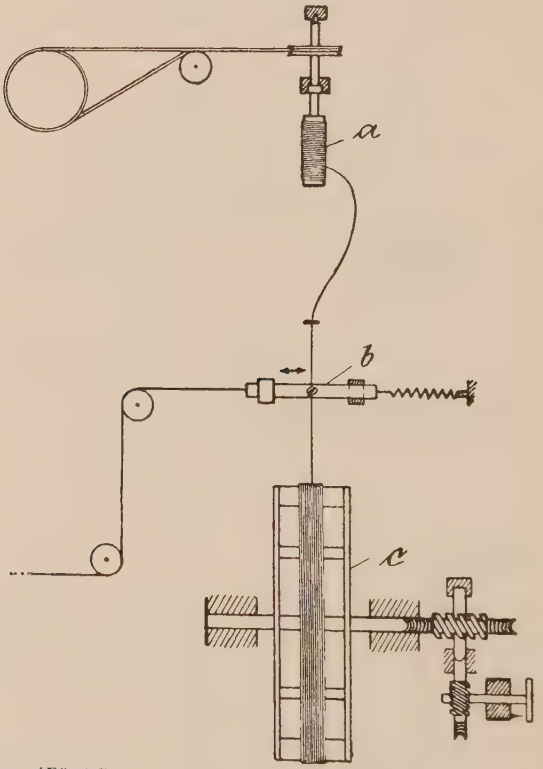
The silk, which is now in the form of hanks, is then subjected to the various special after-treatments, such as denitration, removal of copper, and so forth, which will be described in various later chapters.

We will only refer shortly here to certain operations of a general character, more particularly bleaching, sorting, and numbering, and also to various processes intended to improve the strength, brilliancy, feel, and so forth, of the fibre.

Bleaching. In some works, the silk is soaked before bleaching by treating it in a warm bath at about 60° C. containing Marseilles soap or Monopole soap, for about half an hour, and then introducing it into the bleaching liquid without rinsing. Mitscherling (*Kunststoffe*, 1912, p. 329) recommends a similar

treatment of collodium silk for one hour in neutral soap solution, or a solution of water-soluble oils at 50° C., as a preliminary treatment before bleaching.

Artificial silk is bleached by the same reagents as cotton, and therefore more particularly by hypochlorites (bleaching



(*Fürst G. Donnersmarckschen Kunstseiden- und Acetatwerke*)

Fig. 71. Combined Re-winding, Twisting, and Reeling Machine

powder or sodium hypochlorite), hydrogen peroxide, sodium peroxide, sodium perborate, and so forth.

According to Mitscherling, bleaching powder, although very cheap, is now scarcely used for collodium silk, as not only does it attack the fibre rather strongly, but it also causes the development of a strong yellow colour on storage.

Hydrogen peroxide and per-salts produce excellent bleaching effects, do not attack the fibre much, and do not cause it to become yellow on storage. They are, however, relatively dear. Therefore, the reagent most commonly used is electrolytic bleach (sodium hypochlorite) which is readily prepared by the electrolysis of brine, and is intermediate in properties between bleaching powder and hydrogen peroxide.

Bleaching is usually carried out in the well-known manner in large vats, and the hanks of silk are supported on smooth wooden rods, or better still on glass rods, and are regularly turned in much the same manner as in dyeing.

The bleaching process can also be carried out in closed kiers, such as are recommended, for example, by Escales (*Die Schiessbaumwolle*, 1905, p. 20) for the pre-treatment of cotton. (See also Erban, *Kunststoffe*, 1911, p. 167.) It is stated that complete bleaching is obtained in this manner in about one hour, in a cold bleaching bath, without any mechanical or chemical damage of the fibre. Rinsing, scouring, and soaping can be carried out in the same apparatus.

The addition of soap (neutral Marseilles soap or Turkey red oil soap) to the bleaching vat has a very favourable effect. The bleaching liquor penetrates more thoroughly and the bleaching process is more rapid and very uniform. The handle of the goods is improved in the same manner as by subsequent soaping. Moreover, soaped goods withstand drying at high temperatures distinctly better than if they are not soaped.

After bleaching, the goods are once more soured for a short time with a very dilute solution of sulphuric, hydrochloric, acetic, or nitric acid. With the latter acid or with acetic acid, the peculiar scroop of natural silk can readily be imitated, but sulphuric acid is cheaper and hydrochloric acid offers the advantage that it is particularly easily removed from the fibre by washing, and imparts to the silk a very soft feel or handle.

After souring, the goods are thoroughly rinsed, and may be soaped and again rinsed, and are then dried in a centrifuge, during which process the silk may conveniently be wrapped in cloths in order to protect it from damage. In German patent 367,783, E. Schülke describes a contrivance for the regulation

of the inflow of washing liquids into the centrifuges for washing artificial silk, which is regulated by means of electrically-controlled baffles. A process for continuous washing and after-treatment of artificial silk and similar materials is described by A. Kaempf in German patent 399,666. The hanks are suspended from revolving rollers and dip into the bath situated below ; they are so carried round by the rollers that the washing liquid is carried up by the rising side of the hank approximately to the height of the roller, and then flows back,

(F. Haas, Lennep, Rheinland)

Fig. 72. Tunnel Drier for Hanks

so that no appreciable quantity of washing liquor penetrates to the descending side of the hank. It is alleged that by this process the required effect is produced in a few minutes, whilst by the ordinary method of washing in flowing water, even with a considerable current, many hours are required.

According to German patent 363,100 of H. Wünschmann, a high lustre and great softness are obtained in artificial silk by boiling it under pressure in hank form, or in the piece.

Drying the Artificial Silk Hanks. The drying which now follows is usually carried out on a manufacturing scale in steam-heated drying chambers, through which air is circulated. The hanks are usually introduced into the chambers on movable stands. Various drying ovens for artificial silk are constructed by Friedrich Haas, Lennep, Rheinland. Fig. 72 shows an

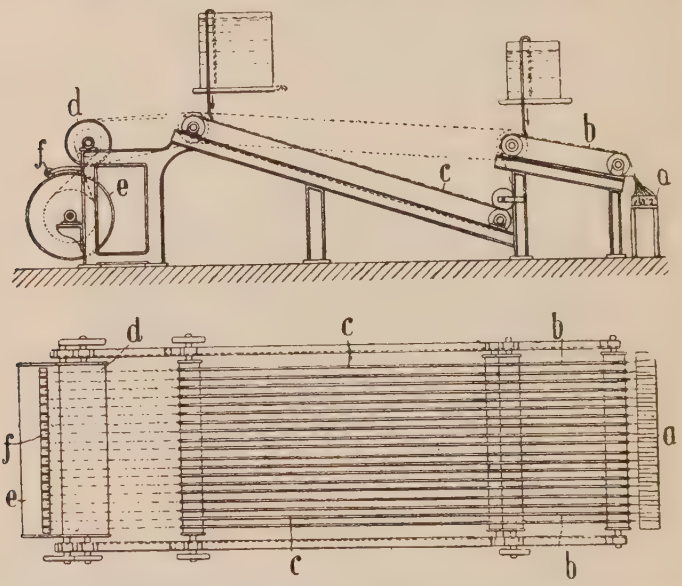
installation of this kind for drying hanks. It is only possible to decide in each case whether it is better to dry for a short time at a high temperature or for a long time at a lower temperature, and whether one should dry with or without tension. The feel of the silk and its lustre in particular, and to a lesser degree its strength and durability, are greatly influenced by the method of drying. Frequently the silk undergoes a preliminary drying under tension before bleaching or otherwise treating chemically, and is then submitted to chemical treatment and finally dried without tension. According to German patent 394,448, W. P. Deaper carries out the final drying in such a manner that the suspended hanks have a limited freedom of movement and are submitted to the action of a stream of hot air of at least 3 to 5 metres per second, which causes the fibre to be soft and loose.

Drying at a higher temperature usually produces a brighter lustre, but it is less favourable to the quality of the fibre. Moreover, the individual threads easily dry irregularly, giving rise to short loops, which are easily broken. Mitscherling (*loc. cit.*, p. 329) proposes to dry hanks, which are to be used in the raw state or merely bleached, at a high temperature, and those which are to be dyed at a lower temperature. It depends, however, on the kind of silk, that is, whether it is collodium silk, viscose silk, and so forth. For example, collodium silk is often dried at 30 to 40° C. only with a moderately strong circulation of air. Direct steam dries the fibre very rapidly, but easily causes it to have a hard feel.

In German patent 312,393, the Elberfelder Glanzstoffabriken describe a rapid drying process for freshly-formed cellulose threads. They found that the threads can be dried in hot air at 100 to 130° C. and over, without damaging the thread, if air or gases inert to cellulose are passed over the goods on the counter-current principle, and if care is taken that contact between the air and the threads shall be as intimate as possible. The process is said to be very suitable for the drying of staple fibre, wool substitute, schappe and similar materials.

Continuous Process. Successful attempts have been made to combine the several operations of spinning, fixing, or other

after-treatment, washing, drying, winding, and doubling, if necessary, in one single working process. In this connection the process of the Vereinigten Glanzstoffabriken Elberfeld developed by Dr. Boos, should be particularly mentioned. (See British patent 16,495/1907, German patent 235,134, Austrian patent 35,269, Swiss patent 41,109, and French



Figs. 73A and 73B. Combined Fixing, Washing, Drying, Winding, and Twisting Machine of Dr. Boos

patent 379,935.) An installation suitable for the application of the process to cuprammonium silk is shown diagrammatically in section in Fig. 73A, and in plan in Fig. 73B.

The threads which emerge from the spinning bath *a*, are first carried over the obliquely-ascending belt conveyer *b*, on which they are sprinkled with dilute sulphuric acid from the container above. They are then carried over the conveying rollers to the larger belt conveyer *c*, on which they are thoroughly washed with water. From here the threads pass on over the drying cylinders *d* and *e*, and are finally wound on the bobbins *f*. Other installations for the same purpose have

been patented by Eck, in German patent 300,254, and, for viscose silk in particular, by Denis, in German patent 342,092.

Mechanical After-treatment. In most works the hanks of artificial silk are subjected to various mechanical treatments, in order to increase the lustre and improve the feel. It is obvious that such operations carried out on so sensitive a material require the greatest care and supervision. If the lustre and the feel are good, it is usually sufficient simply to open the hank by holding it firmly in one hand, whilst the other is passed through the middle of the hank to its other end, and then striking it several times, a process which is repeated at various parts of the hank. The fibres, which adhere somewhat after the drying process, are thus loosened. A similar process is glossing, which also loosens the silk and makes the hank somewhat softer and gives it a better feel. This operation is carried out by hanging the silk on to a smooth fixed bar and twisting it firmly, with simultaneous tension, either with the hand, or better, with a smooth wooden bar, and repeating this manipulation several times at various points of the hank. A form of glazing, such as is used in the cotton industry, is sometimes applied to artificial silk. Calenders are usually used for the purpose, through the rolls of which the material is repeatedly pressed. Polished steel rolls give the best effect, particularly if they are simultaneously steam heated. Such operations should be avoided, however, as far as possible.

Increasing the Strength of Fibre. Artificial silk thread is weaker than real silk, more particularly when moist. Even the strength of natural silk is considerably reduced by moistening, but not to nearly the same degree. Further details will be found in the chapter on the properties of artificial silk. Although, generally speaking, a considerably better thread is now produced than formerly, the problem of avoiding the great reduction in strength of artificial silk on moistening has not yet been solved, although many efforts have been directed to this end. Attempts were first made to overcome the difficulty by certain additions to the spinning solution. A. Chardonnet recommended the addition of turpentine ; Strehlenert

(British patent 22,540/1896) the addition of aldehydes ; and the Société de Tubize (French patent 361,690) the addition of ethereal oils. Bardy believed that he had solved the problem by a process of parchmentizing the thread (French patent 313,464, and *Monit. Scientif., Choix de Brevets*, 1903, p. 57), by treating the silk at 15 to 20° C. with sulphuric acid which had been diluted with an equal volume of water. According to British patent 21,144/1906, and French patent 369,957, E. W. Friedrich attempts to obtain the same result by treating the fibres with strong dehydrating agents, such as alcohol, ether, carbon disulphide, benzene, and so forth, in vaporous or gaseous form. The removal of water may possibly increase the strength of the fibre slightly, but it also reduces its elasticity. The opinion that by this means hydro- or polyhydrocellulose is reconverted into simple cellulose, cannot be entertained. The process is of no more practical importance than the composition of the spinning bath, claimed in the same patent. The same idea is the basis of German patent 134,312 of E. Thiele, who proposes to dehydrate the silk, after drying, by treatment with dehydrating agents such as calcium chloride, alcohol, and so forth. The otherwise rational proposal of J. Gebauer (in British patent 30,510/1909, German patent 232,605, French patent 403,264, and the patents of addition, German patent 235,220, French patent 11,164), to impregnate the fibre with india-rubber, and subsequent vulcanization, which may be preceded by treatment with albumen solution, is technically impossible on account of the very great increase in the cost of the fibre which would thus be caused. The so-called " sthenose " process of Eschalier (British patent 25,647/1906, German patent 197,965, French patent 374,724, and patent of addition 8122, Austrian patents 40,067 and 40,080, and the further French patents of addition 9904 and 10,760), which was specially devised for application to viscose silk, has not been technically adopted.

According to this process, the artificial silk, in hanks, or in the form of woven goods, is first soaked in a solution containing an aldehyde, which may suitably be formaldehyde, and an acid or substance of acid reaction such as acetic acid or lactic acid, and the solution is then

dried on the fibre in a drying chamber, if necessary at a high temperature, and the material rinsed and re-dried. According to the last-mentioned French patent of addition, the best results are obtained with aldehyde and acid, more particularly in acetone solution. For example, for 10 parts of dry silk, a bath is to be used consisting of 150 to 200 parts of acetone, 5 to 20 parts of 40 per cent formaldehyde and 0·50 to 0·15 parts of sulphuric acid (66° Bé) or hydrochloric acid of 20 to 23° Bé. The material is to be dipped into the bath and boiled therein for 3 to 5 hours under reflux. It is then to be washed with water and dried. Acids other than sulphuric or hydrochloric acid may be used, in so far as they do not destroy the other chemicals or attack the silk fibre. By the Sthenose process a distinct increase in strength was produced in the dry fibre, but more particularly in the wet fibre. The process is, however, too complicated and dear for large scale application, and its effect is too uncertain, as it is difficult to carry out and difficult to avoid too great a reduction of the elasticity and extensibility of the fibre.

In German patent 414,523, the Textile Ausrüstungs-Gesellschaft, Crefeld, proposes to submit artificial silk to the action of aluminium nitrate solutions, which may be followed by a further treatment with alkali silicates or soaps, in order to improve the fibre and reduce its sensitiveness to water. This is naturally accompanied by a weighting effect on the silk.

According to French patent 434,602, of Bourgeois, Nieuviarts and de Clercq, artificial silk threads are made waterproof by passing them through a bath of petroleum. The process would be simple and cheap if the thread were made permanently waterproof, and if the process did not suffer from other disadvantages, such as a bad odour, and so forth.

In British patent 9196/1915, Swiss patent 74,231, and French patent 477,655, the Soc. la Soie Artificielle proposes to increase the resistance of artificial silk to water by treating it with formaldehyde or trioxymethylene in presence of ferric chloride or an organic acid, and if necessary also with a dehydrating agent, such as alum or calcium chloride ; for example, the hanks are to be treated with formaldehyde and ferric chloride, dried *in vacuo*, and heated in a steam bath. If any effect is produced, it is so small that it would not justify the cost of the process.

According to A. Chesnais' French patent 463,693, hypophosphorous acid or its salts increase the strength of artificial silk when wet, by reducing its power of absorbing water (by dehydration of the molecule) whether added to the spinning solution or to the spinning bath, or if the silk is subsequently treated with them.

L. Fessmann, in German patent 316,045, claims to produce the same effect, the diminution of the power of absorbing water, by consolidating the fibre substance ; for example, by passing the thread between steel rollers at high pressure in very thin layers, so that the consolidation may be as complete as possible. He has mainly staple fibre in mind. Neither process is of any practical importance. The mechanical treatment by the last-named process in particular, damages the fibre to a great extent, so that any good effects may be nullified.

The process proposed by L. Meyer, in German patent 314,968, is

similar to the usual process of rendering fabrics watertight. In order to prevent the adherence of the fibres through the action of metallic soaps in the ordinary treatment with metallic salts and soaps, he soaks the fibre in solutions of metallic salts, dries it, and then treats it with alkaline reagents. Finally, he treats it with soap solution in order to attain a soft handle.

The process described in British patent 116,103 of the Auer-Gesellschaft consists essentially in precipitating metallic hydroxides on to the fibre by means of ammonia or other gases of alkaline reaction.

A very remarkable process is proposed by S. Culp in German patent 274,044. He claims to thicken fibres of either natural or artificial silk by exposing them in a suitable vessel to the evolution of gas, which is provided, for example, by precipitating calcium carbonate on or in the fibre and decomposing this precipitate with dilute acids. It is stated that the same result may also be attained by the introduction of carbon dioxide.

Sorting and Numbering. Before the silk is ready for sale or for treatment in the dye works, it must be sorted according to quality and number (that is, thickness of thread). In sorting for quality, each hank is hung on a wooden block, and goods of first quality then show a high lustre, pure white colour, cleanliness (that is, the absence of spots, other defects, or broken threads), and must also have a soft, silky feel, and consist as far as possible of a single unknotted thread. All hanks in which one or other of these properties is missing, or only present to a lesser degree, are classified as goods of second or third quality, or are even rejected. Sorting is a very difficult operation, which should only be entrusted to able, experienced, and reliable workmen. The strength of the silk is also tested on samples ; further details will be found in the chapter on the properties of artificial silk, page 353 *et seq.*

After the hanks have been sorted into qualities, their number or titre must be determined. Since the introduction of correctly working spinning pumps, already described (see page 88 *et seq.*) it is unnecessary to weigh the individual hanks, but it is sufficient to weigh a few samples, and further to weigh a large number of hanks of the same titre as a sort of control.

Number or Titre. The metric or international titre, which is also legally accepted in Germany, is described in deniers (ds.), namely, the number of grammes contained in a thread 10,000 metres long. In practice the hanks are usually 900 metres

long, as in the case of real silk, and it is therefore simpler, as for real silk, to consider as one denier the weight of a thread 9000 metres long. This is the so-called Italian, or legal titre. If, for example, a hank 900 m. long weighs 8 gm., its number is 80 ds.

The size of thread, number, or titre, is simply determined by determining the weight of a 900 metre hank, and multiplying by 10 ; this gives the titre. The titrating balances are constructed like letter balances, but with a hook for suspending the hank, and have a scale with a pointer which usually reads the titre directly in deniers.

This method of numbering takes a comparatively long time. Even a clever and industrious worker cannot weigh more than 7 or 8 hanks per minute, or about 4000 hanks in an eight-hour day ; or 40 kg. of silk of an ordinary titre of 100 deniers. Titrating machines have therefore been constructed which automatically sort the hanks according to titre. (See Becker, *Die Kunstseide*, 1912, p. 85.)

We have now followed the process of manufacturing artificial silk up to the point where the product leaves the works in order to be dispatched to the dye works, finishing works, weaving shed or elsewhere.

For reasons already mentioned, the dyeing, finishing, and weighting of artificial silk will be discussed in a special chapter in connection with the further treatment and use of this article.

CHAPTER IX

COLLODIUM SILK

Having become acquainted in the preceding sections with the manufacture of artificial silk in general, we will now turn to the individual processes of manufacture. From the description of the historical development of the industry in the first chapter we have already learnt that so far four principal processes of manufacture of artificial silk are technically employed: the collodium, cuprammonium, viscose and acetyl-cellulose processes. A fifth process, the cellulose ether process, may possibly attain greater importance within a measurable time. We will now consider these individual processes singly, and will then briefly discuss a few other processes which are not without interest, although they have never attained permanent technical success.

PRODUCTION OF COLLODIUM SILK

(Chardonnet Silk)

Collodium silk, wrongly called "nitro silk," is the oldest form of artificial silk, as has been seen in the section on the historical development of the industry. Its manufacture involves the following phases—

1. The production of cellulose nitrate by the nitration of cellulose.
2. The production of collodium by dissolving cellulose nitrate.
3. The production of the thread by spinning the collodium solution.
4. The denitration and further treatment of the thread to produce the finished article.

Production of Cellulose Nitrate

Raw Material. The raw material for collodium silk is almost exclusively cotton in the form of linters, and especially of spinning waste (see pages 30 and 31), which are purified and

pre-treated by the methods described on page 61 *et seq.* Lunge and Bebie (*Zts. f. angew Chem.*, 1901, p. 565), nitrated various varieties of cotton, namely, chemically pure absorbent cotton, American cotton (middling fair), Florida cotton, white Egyptian Abassi cotton, and yellow Egyptian cotton, under identical conditions, and were unable to discover any noticeable difference either in the nitrogen contents, solubility or yield, so that the various varieties behaved identically. This view appears to be in conflict with the statement of Guttmann (see *Escales, Nitrocellulose*, p. 156), that too thorough a purification of cotton, such as occurs in the preparation of chemically pure absorbent cotton, causes the cotton to ball together during nitration, and consequently uneven nitration. Mitscherling (*Kunststoffe*, 1912, p. 261) also found definite differences, more particularly between Russian and American cotton. It is, however, possible that the degree of bleaching which the absorbent cotton used by Lunge and Bebie had undergone was of an entirely different order from that of the cotton used by Guttmann or Mitscherling, for an influence of this kind caused by the degree of bleaching would correspond to the general behaviour of cottons, which differ in this way, for example, with regard to solution in cuprammonium solutions or conversion into viscose. In conformity with this view, Piest (Piest, Stich and Vieweg, *Das Celluloid*, 1913, p. 34), states that nitro-celluloses manufactured from more strongly bleached cotton show a greater solubility in ether-alcohol, form more mobile solutions, and are more difficult to stabilize. In his German patent 56,655, Chardonnet states that, in general, cellulose which has previously been bleached does not form a stiff collodium suitable for the preparation of fibres. Similarly, Cross, Bevan, and Jenks (*Ber. d. Chem. Ges.*, 1901, p. 2498) found in their experiments on the action of sulphuric acid in the nitration bath that essential differences existed in the nitration of unbleached and bleached cotton. It has already been suggested (page 54) that this influence of bleaching may be caused by a partial superficial oxidation and hydrolysis.

The question of absorptive power, which has also already

been referred to (page 56) is of special importance for the nitration process, as it is obvious that the rapidity, and more particularly the uniformity, with which the acid penetrates the cellulose plays a large part in the production of a uniform product. Cotton rags, which are very absorptive, usually nitrate very well for this reason. Linters and spinners' waste, which are often strongly compressed during transport, must be thoroughly opened. Cotton papers should be as thin as possible and of the character of blotting paper, that is, they should be as absorbent as possible.

Wood-pulp in the form of crinkled or tissue paper can very readily be converted into cellulose nitrate, and was largely used during the war for the production of explosives. In the collodium silk industry, however, the use of wood-pulp has not so far been successful, as on the one hand the nitration of cotton is easier and more certain, and on the other hand only relatively small quantities of collodium silk are now manufactured, so that the requirements of raw material are readily covered by spinners' waste, linters, and so forth. According to F. Nettleford (*Chemical News*, Vol. 55, p. 306), the nitration of wood-pulp takes place otherwise than that of cotton. With the same nitration acid, he obtained from wood-pulp a product containing 11·2 per cent of nitrogen and 41·6 per cent of soluble matter, whereas from cotton he obtained the highest degree of nitration and a solubility of 8 per cent only.

We may refer here to the general discussion on page 61 *et seq.* on the pre-treatment of the raw material and the effects of variations in the same, and will now mention certain special processes of pre-treatment of cellulosic material destined for nitration.

As described in German patent 64,031, Chardonnet had already discovered that high temperatures exert a favourable influence on the cellulosic material, by decomposing the encrusting impurities and thus assisting their subsequent removal, and also by altering the cellulose itself in such a manner that the nitrated products show an appreciably better solubility, and that it is easily possible, for example, to obtain

a 20 to 25 per cent collodium solution. For this purpose he heats the cellulose material, for example, for 4 to 8 hours at a temperature of 150 to 170° C. In a similar manner, and according to German patent 199,885 and Austrian patent 37,030, Berl heats the cellulose before nitration in presence of inert gases free from oxygen, such as flue gases, water gas, carbon dioxide, nitrogen or superheated steam, to relatively high temperatures. For example, he heats cotton in the manner described for 4 days to 120° C., and nitrates it under similar conditions alongside a sample which has been heated for 6 hours to 100° C. only. He found that both cellulose nitrates showed the same percentage of nitrogen, namely 13·5 per cent, but that the nitrate obtained from the sample dried at 100° C. furnished a solution the viscosity of which was 80 times as high as that of the other sample. He states that no undesirable changes were noticeable in the more highly-heated sample, and that the yields were the same in both cases. The considerable reduction in the viscosity indicates a fairly considerable depolymerization of the cellulose molecule.

Theoretical Considerations on Cellulose Nitrates. Cellulose nitrates or nitric acid esters are usually, but wrongly, described as "nitrocelluloses." They are, in fact, true, saponifiable nitric acid esters, the nitrogen atoms of which are not united to the carbon of the cellulose molecule as in the unsaponifiable nitro-compounds, but are attached, as in all esters, to an intermediate oxygen atom. The following structural formulae will make the difference clear—

$\equiv C—O—NO_2$	$\equiv C—NO_2$
Nitric acid ester	Nitro-compound

In general, cellulose nitrates are produced by treating cellulose with a mixture of strong nitric and sulphuric acids, the so-called nitration mixture. According to the composition of the nitration mixture, and also according to the duration and temperature of the reaction and to the proportions of acid to cellulose, various cellulose nitrates or mixtures of the same are produced during nitration, namely, the mono-nitrate $C_6H_9O_4 \cdot ONO_2$, di-nitrate $C_6H_8O_3(ONO_2)_2$, tri-nitrate $C_6H_7O_2(ONO_2)_3$, and so forth, up to the hexa-nitrate.

Technically, two main varieties of cellulose nitrates can be distinguished—

1. Collodium cotton or celloxylin, which is a mixture of mono-, di-, and tri-nitrate containing 11 to 12·5 per cent of nitrogen. These nitrates are easily soluble in ether-alcohol.

2. Gun-cotton or pyroxylin, consisting of higher nitrates and containing more than 12·5 per cent of nitrogen. In contrast to collodium cotton, this product is usually insoluble in ether-alcohol. In practice, gun-cotton always contains smaller admixed amounts of lower nitrates, that is, of collodium cotton.

It is, of course, obvious that no sharp boundary can be drawn between these two classes of cellulose nitrates, more particularly as the nitration products almost always consist of mixtures of various nitrates. Moreover, easy solubility does not always go hand in hand with low nitrogen contents. It is true that nitrates containing but little nitrogen—apart from extremely weakly nitrated products—are always soluble, and that the insoluble gun-cottons have always a high nitrogen content ; but, of course, this does not imply that all nitrates with a high nitrogen content are insoluble. In actual fact, for example, Lunge and Bebie (*Zeitschr. f. angew. Chem.*, 1901, p. 513) prepared both a soluble and an insoluble cellulose nitrate, both of which showed a nitrogen content of about 12·8 per cent, corresponding to deka-nitrocellulose (C_{24} . . .), and according to their directions H. Roscoe also obtained the same results. Finally, according to a communication in the *Journal of the Society of Chemical Industry*, 1900, p. 315, soluble products have been obtained containing 13·2 per cent of nitrogen.

Stages of Nitration. We must here say something on the various stages of nitration. The nitrogen contents of the cellulose nitrates which are produced, vary greatly according to the conditions under which the nitration is carried out, from 6·7 per cent to more than 14 per cent. It was therefore assumed that a considerable number of stages of nitration must exist and the formulae were referred to a multiple of the $C_6H_{10}O_5$ formula of cellulose, as is still frequently done. Thus, Eder (*Ber. d. Chem. Ges.* 13, p. 175) based the formulae of cellulose

nitrates on the double cellulose formula $C_{12}H_{20}O_{10}$. He gives the following formulae and percentages of nitrogen—

Hexanitrate	$C_{12}H_{14}O_4(NO_3)_6$	14·14 per cent N.
Pentanitrate	$C_{12}H_{15}O_5(NO_3)_5$	12·75 ,, ,, ,,
Tetranitrate	$C_{12}H_{16}O_6(NO_3)_4$	11·11 ,, ,, ,,
Trinitrate	$C_{12}H_{17}O_7(NO_3)_3$	9·15 ,, ,, ,,
Dinitrate	$C_{12}H_{18}O_8(NO_3)_2$	6·76 ,, ,, ,,

Vieille (*Compt. rend.*, 1882, p. 132) and Lunge (*loc. cit.*, p. 484) refer the nitrates to the four-fold cellulose formula $C_{24}H_{40}O_{20}$. They mention the following stages of nitration—

Dodeka-nitrocellulose	$C_{24}H_{28}O_8(NO_3)_{12}$	14·14 per cent N.
Endeka- ,,	$C_{24}H_{29}O_9(NO_3)_{11}$	13·47 ,, ,, ,,
Deka- ,,	$C_{24}H_{30}O_{10}(NO_3)_{10}$	12·75 ,, ,, ,,
Ennea- ,,	$C_{24}H_{31}O_{11}(NO_3)_9$	11·96 ,, ,, ,,
Octa- ,,	$C_{24}H_{32}O_{12}(NO_3)_8$	11·11 ,, ,, ,,
Hepta- ,,	$C_{24}H_{33}O_{13}(NO_3)_7$	10·18 ,, ,, ,,
Hexa- ,,	$C_{24}H_{34}O_{14}(NO_3)_6$	9·15 ,, ,, ,,
Penta- ,,	$C_{24}H_{35}O_{15}(NO_3)_5$	8·02 ,, ,, ,,
Tetra- ,,	$C_{24}H_{36}O_{16}(NO_3)_4$	6·76 ,, ,, ,,

Mendelejeff (*Moniteur Scientifique*, 1897, p. 510) went still further, and found it necessary to represent cellulose nitrates on the basis of a cellulose formula, $C_{48}H_{80}O_{40}$, as he obtained a nitrate soluble in ether-alcohol containing 12·44 per cent N, a figure midway between the deka- and ennea-nitrocelluloses of Vieille, the former of which he had described as insoluble and the latter as soluble in ether-alcohol.

It cannot, however, be assumed that any of these formulae correspond with the true molecular size. The molecular weight is unknown, and also, as already mentioned, one is presumably always dealing with mixtures of products of various degrees of nitration, with the possible exception of the most highly nitrated compounds which have been obtained with nitric anhydride, and which possibly represent a homogeneous nitrate. It is obviously most convenient to avoid any unnecessary complication and to choose the simplest formulae which will represent the experimental facts. There is no reason not to use the simplest cellulose formula, $C_6H_{10}O_5$, as the basis of those of the cellulose nitrates. This is often done (see, for example, Heuser, *Lehrb. d. Cellulosechemie*, 2nd Edn., p. 35 ; Meyer and Jacobson, *Organische Chemie*, 1923, p. 1045, and others), but not always. In the absence of any recognized system, it is

necessary to indicate in some manner the cellulose formula to which the nitrate is referred, for example, by writing hexanitrocellulose (C_{24} . . .).

Collodium cotton to be used for artificial silk must always be completely soluble, and should contain as little nitrogen as possible ; that is, it should be free from gun-cotton. The nitration process, which naturally determines the character of the nitrate, must be adjusted for this purpose.

Theory of Nitration. The so-called nitration of cellulose is a true ester formation, and consequently reversible. The cellulose nitrate obtained, for example, according to the equation

$$C_6H_{10}O_5 + 3HNO_3 = C_6H_7O_2(ONO_2)_3 + 3H_2O$$

can be saponified to form cellulose hydrate and nitric acid by the addition of water. In actual nitration, this absorption of water actually occurs owing to the excess of acid, more particularly sulphuric acid. In presence of the large excess of nitration acid it does not, of course, lead to the re-formation of the original cellulose, but merely to the production by saponification of lower nitrates from higher nitrates. In other words, a state of equilibrium is established for which the following equation holds, in accordance with the effect of mass action—

$$\frac{(\text{Ester}) \,.\, (\text{Water})}{(\text{Cellulose}).(\text{Acid})} = K$$

The terms in brackets indicate concentrations of the respective substances. It may be assumed that this state of equilibrium is attained when the quantity of ester produced in a given time is equal to the amount which is saponified. Such a condition of equilibrium corresponds to a definite state of nitration or to a definite mixture of neighbouring stages of nitration, which, as is clear from the equation, would correspond to a lower or higher total degree of nitration, that is, to a lower or higher percentage of nitrogen, according to the ratio of water to acid. In accordance with this standpoint, Berl and Klaye (*Zts. f. d. ges. Schiess- u. Sprengstoffwesen*, 1907, p. 403) find as a result of their investigations that each nitration mixture corresponds to a definite cellulose nitrate and that an equilibrium condition is established between ester and acid. This is,

of course, only true for a definite uniform temperature. By greatly reducing the temperature, for example, the saponification, that is, the course of the first reaction from right to left, can be repressed, and on the other hand, by raising the temperature and by a sufficiently long time of reaction, it can be converted into the main reaction, in which case almost the whole of the esters which are formed are re-saponified.

The further experimental results of Lunge and Weintraub, and of Lunge and Bebie agree with this view. According to these, the degree of nitration, that is, the percentage of nitrogen in the nitrated mixture, is, within certain limits, essentially determined by the percentage of water in the nitration acid only. In consequence of the reverse reaction, the saponification of the esters, the equilibrium condition cannot normally correspond to the maximum nitration, that is, to the introduction of twelve nitrate groups in the C_{24} formula, corresponding to 14·14 per cent N, in a nitration bath containing water. Berl and Smith (*Ber. d. Chem. Ges.*, 1908, p. 1837) are therefore quite correct when they attribute the fact that the highest stages of nitration were not attained, to the saponifying action of the nitration mixture. In this connection, the production of higher nitrates containing up to 13·9 per cent N by nitration with nitric anhydride is of interest. (See Hoitsema, *Zts. f. angew Chem.*, 1908, p. 173). In this case water, which is essential for the saponification process, is absent.

The Nitration Acid. By careful work, utilizable cellulose nitrates can be obtained by nitric acid alone, if this is sufficiently concentrated. Very dilute nitric acid only effects hydrolysis or oxidation on warming. In his communication on a labile nitrate of cellulose (*Ber. d. Chem. Ges.*, 1904, p. 549), E. Knecht states that he obtained a nitrate with 65 per cent nitric acid of specific gravity 1·14, which contained one molecule of nitric acid per molecule of $C_6H_{10}O_5$. This compound was, however, so labile that it was completely and immediately decomposed by water only. Lunge and Bebie (*Zts. f. angew Chem.*, 1901, p. 483) observed but very weak nitration by the use of acids of this concentration, as the product which they obtained contained 1·3 per cent of nitrogen only, whereas the

mono-nitrate would contain 6·7 per cent of nitrogen. More highly concentrated acids, from about 80 per cent HNO_3 upwards, but more especially 90 per cent and stronger acids, produce highly nitrated products, which contain up to 13·5 per cent of nitrogen, according to Hake and Bell. According to these results, former assumptions (Escales, *Die Schiessbaumwolle*, 1905, p. 157 ; Berl and Smith, Jr., *Ber. d. Chem. Ges.*, 1908, p. 1837) that with pure nitric acid nitration can only proceed as far as the dekanitrate (in terms of $C_{24}H_{40}O_{20}$) can no longer be upheld. Such highly concentrated acids, however, also act as strongly gelatinizing, mercerizing, and parchmentizing agents, and if a sufficient excess of nitric acid is present, may even dissolve the cellulose. The nitric acid esters are, therefore, not then produced in a technically useful form, but either as a strongly swollen, slimy mass, which can hardly be washed, or in the form of viscous solutions from which the compounds are precipitated on dilution with water in the form of more or less voluminous flocks. For these reasons, nitration with nitric acid alone is not technically employed. On the other hand, utilizable products are obtained by nitration with a mixture of sulphuric and nitric acids, which is commonly known as nitration acid.

The action of the sulphuric acid during nitration may be of several kinds. On the one hand, it presumably acts as a powerful fixing agent for the water which is either formed during the reaction or is initially present, and thus prevents too great a dilution of the nitric acid. In fact, if nitration only occurs when the nitric acid is present as anhydrous mono-hydrate (HNO_3), or at least as $HNO_3 \cdot H_2O$, as Saposchnikow states (*Zts. f. d. ges. Schiess- u. Sprengstoffwesen*, 1906, p. 453), then Kullgren's view (*loc. cit.*, 1908, p. 146) should be essentially correct, namely, that the action of the sulphuric acid in the nitration bath consists in the decomposition of the higher stages of hydration of nitric acid ($HNO_3 \cdot H_2O$ and $HNO_3 \cdot 3H_2O$), the existence of which was proved by Küster and Kremann (*Zts. anorg. Chem.*, 1904, p. 1). Cross, Bevan, and Jenks (*Ber. d. Chem. Ges.*, 1901, p. 2496) attribute another function to the sulphuric acid in the nitration bath. These investigators

isolated cellulose nitrates containing sulphuric acid to the amount of 4·62 per cent, that is, mixed nitric-sulphuric acid esters, the sulphuric acid radicle in which could readily be removed by water or by aqueous acetone. From these results they came to the conclusion that during nitration such mixed nitric-sulphuric acid esters are always the first products of the reaction, and that they are only converted into pure nitric acid esters by washing with water and consequent liberation of the sulphuric acid radicles. It is doubtful whether this conclusion can be accepted as universally true, or whether the formation of sulphuric acid esters or mixed esters may not, perhaps, be considered merely as an unimportant by-reaction in which relatively few of the cellulose molecules take part.

We have, however, already mentioned (pages 169 and 170) that concentrated nitric acid alone does not merely nitrate, but also acts as an oxidizing and hydrolizing agent, and more particularly as a gelatinizing agent and even as a solvent for the cellulose. These actions of nitric acid are prevented by the sulphuric acid, and in consequence the presence of this latter acid may quite considerably increase the yield under otherwise similar conditions.

The use of sulphuric acid in nitration mixtures also leads to other technical advantages of some importance. By its use the quantity of relatively dear nitric acid can be appreciably reduced and the regeneration of the acid can be more satisfactorily carried out. The moist cellulose nitrate contains appreciably less nitric acid after being centrifuged. The mixture of nitric and sulphuric acids attacks both cast and wrought iron comparatively slightly, so that plant and transport containers of iron can be used, and storage in iron tanks is considerably simpler and less dangerous than the storage of nitric acid alone.

Factors which Influence the Nitration. The quality and quantity of the raw material, the qualitative and quantitative composition of the nitration bath, the relative proportions of cellulose and nitration acid, the temperature and duration of the nitration and other factors, all play a part in varying degrees in the results of the nitration.

Influence of the Raw Material. The influence of the source and origin of the raw material on the course of the nitration has already been referred to (see page 163). We must also mention that the nitration process is influenced not only by the relative proportion, but also by the absolute quantity, of cellulose which is used. This is presumably mainly due to the varying amounts of heat of reaction, which can more readily be removed from small than from larger batches. This fact is important in transferring laboratory experiments to the manufacturing scale. As is frequently the case in chemical processes, the results obtained on a small scale do not indicate what will happen under large scale conditions. As, however, it is usual in practice to work with a relatively large excess of nitration acid, changes in the proportion of cellulose to acid do not exert much influence unless they are very extreme. Lunge found that alteration of the proportion of cellulose to acid from 1/30 to 1/12 caused a reduction in the nitrogen contents of the cellulose nitrate corresponding to 5 c.c. of NO. The proportions of cellulose to nitration acid used in technical practice vary greatly. Piest (*Das Celluloid*, 1913, p. 31) states that the usual proportion is 1/50 to 1/60.

Influence of the Composition of the Nitration Bath. *Proportions of the Two Acids.* If one takes as standard a bath containing equal quantities of sulphuric and nitric acids (calculated as anhydrous, H_2SO_4 and HNO_3), and compares with this baths containing higher proportions of sulphuric acid, then, as shown by Lunge and Bebie (*Zts. f. angew Chem.*, 1901, p. 508), one first observes an increase in the nitrogen contents of the nitrate, until the proportion of sulphuric to nitric acid is 3/1. When the proportion of sulphuric acid was further increased, the increase in the nitrogen contents was barely noticeable. The limit corresponding to complete nitration corresponded to a proportion of about 7/1, and if the proportion of sulphuric acid was further raised an increasing proportion of cellulose was unattacked. When the proportion of sulphuric acid was 8/1, 10·7 per cent was unattacked, and when it was 10/1, 41·1 per cent of cellulose was unattacked, even after remaining in the nitration acid for months.

Moreover, an increase in the proportion of sulphuric acid in the nitration bath caused a considerable retardation of the nitration process, as found by Lunge and Weintraub (*Zts. f. angew. Chem.*, 1899, p. 488), confirming earlier results by Vieille. The structure of the resultant cellulose nitrate is also very greatly influenced by the proportions of the two acids. Nitration baths containing much sulphuric acid lead to a product which disintegrates on drying to a finely fibrous powder, whilst with baths containing nitric acid, either pure or mixed with relatively small proportions of sulphuric acid, the cotton completely retains its original structure but becomes considerably stronger in consequence of shrinkage of the individual fibres.

Water Contents of the Nitration Bath. Lunge and Bebie (*Zts. f. angew. Chem.*, 1901, pp. 488 and 507) carried out detailed investigations and found that the degree of nitration, that is, the nitrogen contents of the nitrated product and more particularly its solubility in ether-alcohol, is determined within certain limits by the proportion of water to acid only, and that the nitrogen contents of the product increase with diminishing proportions of water in the bath. Further, Berl and Klaye have shown that on subsequently adding water to the bath the proportion of nitrogen in the product is reduced according to the equilibrium required by the equation given on page 168, until the equilibrium corresponding to the new composition of the bath is attained. This action of water in the nitration bath, of reducing the nitrogen contents, is, however, only observed when the water contents of the bath exceed about 13 per cent ; at least, the table communicated by Lunge and Bebie in *Zts. f. angew. Chem.*, 1901, p. 514, shows that with water contents in the bath varying from 1·87 to 11·2 per cent, the product has a practically constant nitrogen content, varying from 13·51 to 13·61 per cent. It is only when the water contents reach 13·2 per cent that a definite reduction in the nitrogen contents occurs to 13·25 per cent. This result agrees with those obtained by Lunge and Weintraub (*Zts. f. angew. Chem.*, 1899, p. 473 *et seq.*), which are reproduced in the table given on the next page.

In this case also, as the table shows, the nitrogen contents are only very slightly reduced from 13·65 to 13·21 per cent by increasing the water contents in the nitration acid very considerably, from 5·62 to 11·38 per cent. The table shows especially clearly the considerable influence of the water contents on the solubility of the cellulose nitrate in ether-alcohol, the optimum of which corresponds to water contents of 18 to 19 per cent.

Mathematical Formulae for the Nitration Bath. Several attempts have been made to express the relationship between

Experiment	Nitration mixture			Yield	Solubility in ether-alcohol	Per cent nitrogen in product
	H_2SO_4	HNO_3	H_2O			
1	45·31	49·07	5·62	177·5	1·50	13·65
2	42·61	46·01	11·38	176·2	5·40	13·21
3	41·03	44·45	14·52	—	22·00	12·76
4	40·66	43·85	15·49	167·0	60·00	12·58
5	40·14	43·25	16·61	159·0	99·14	12·31
6	39·45	42·73	17·82	153·0	99·84	12·05
7	38·95	42·15	18·90	156·5	100·02	11·59
8	38·43	41·31	20·26	144·2	99·82	10·93
9	37·20	40·30	22·50	146·0	74·22	9·76
10	36·72	39·78	23·50	138·9	1·15	9·31
11	35·87	38·83	25·30	131·2	0·61	8·40
12	34·41	37·17	28·42	—	1·73	6·50

the nitration effect and the composition of the bath by means of a mathematical formula, from which it should be possible to calculate the necessary composition of the bath for any desired degree of nitration.

Kisniemsky (*Mém. des poudres et Salpètres*, Vol. 10, p. 64) expressed the composition of the nitration mixture by the simple formula—

$$1 \cdot N_2O_5 \cdot H_2O + a \cdot SO_3 \cdot H_2O + cH_2O$$

and called the quantity $1 + a - c = \mu$, the characteristic of the mixture. He states that when μ is greater than zero, only slightly soluble, highly-nitrated products are produced, whilst a bath, the characteristic μ of which is less than zero, is stated

to form readily soluble nitrates with a nitrogen content which becomes larger the less μ exceeds the value -1. Lunge (*Zts. f. angew. Chem.*, 1901, p. 538) found that in general the results of his experiments agreed with this formula. He points out, however, that these values are no longer reliable when μ is in the neighbourhood of zero, that is, between $-0{\cdot}3$ and $+0{\cdot}3$, namely, within an interval which includes a large number of practically important cases. But he found that in other cases also, the conclusion with regard to the result to be obtained is so indefinite that nitrations could hardly be carried out on this basis on a large scale.

A somewhat more complicated formula was given by L. Clément in his theoretical investigations on nitration baths (*Le Caoutchouc et la Guttaperche*, Vol. 6, pp. 3185 and 3269; see also *Kunststoffe*, 1912, p. 384), according to which the required nitrogen contents of a nitration bath could be calculated for any required degree of nitration in accordance with the principles established by Lunge and Bebie. This formula is as follows—

$$Z = \frac{140a - 4{\cdot}5\,\frac{An}{B}\cdot a - 180\,\frac{An}{B}}{4{\cdot}5\,\frac{An}{B}}$$

Z is the required water contents; n the required degree of nitration in percentages of nitrogen; A the weight of nitrocellulose produced, and B the weight of the unused bath. He calls the proportion $\frac{A}{B}$ the nitration modulus. This ratio shows the quantity of cellulose nitrate to be expected per kilogram of the bath; so that, for example, when using 100 kg. of nitration bath per kg. of cellulose nitrate, the value $\frac{A}{B} = 0{\cdot}01$. When producing cellulose nitrate for artificial silk this value is usually somewhat higher, namely, about 0·015. a is the amount of water formed during nitration, and is therefore equal to the amount of water finally present, Z^1, reduced by the initial quantity of water Z; thus $a = Z^1 - Z$.

It is possible to calculate a from experimental nitrations in

which Z, $\frac{A}{B}$ and m, the sulphuric acid concentration, x, and the nitric acid concentration, y, are known, by inserting the values of Z, $\frac{A}{B}$ and n in the above equation and solving it for a. In this way, Clément calculated the values of a for a series of experiments which have been communicated by Lunge, Berl and Klaye, and by Vignon, and compiled the following table—

No.	x	y	Z	n	$\frac{A}{B}$	a	
1	63·35	25·31	11·34	13·89	0·0181	0·417	Lunge
2	43·62	44·88	11·50	13·60	0·0210	0·481	Berl and Klaye
3	41·03	44·65	14·52	12·76	0·0168	0·393	Lunge
4	40·19	43·25	16·61	12·31	0·0166	0·371	,,
5	40·92	41·64	18·00	12·00	0·0151	0·439	Berl and Klaye
6	63·84	16·96	19·20	11·76	0·0225	0·507	Lunge
7	66·37	13·04	20·59	11·66	0·0068	0·154	,,
8	38·95	42·15	18·90	11·59	0·0156	0·344	,,
9	59·77	20·94	19·20	11·54	0·0274	0·007	,,
10	62·52	16·46	21·02	11·23	0·0085	0·187	,,
11	62·52	16·46	21·02	11·00	0·0210	0·457	,,
12	58·88	19·60	21·52	10·96	0·0100	0·217	,,
13	38·43	41·31	20·26	10·93	0·0153	0·326	,,
14	35·91	40·64	19·85	10·70	0·0190	0·393	Berl and Klaye
15	64·85	14·90	30·55	10·53	0·0284	0·590	L. Vignon
16	38·95	42·15	18·90	10·51	0·0610	1·238	Lunge
17	37·20	40·30	22·50	9·76	0·0146	0·286	,,
18	33·72	39·78	23·50	9·31	0·0143	0·272	,,

For the 18 experiments included in this table, Clément also calculated the values k which a assumes when $\frac{A}{B} = 0{\cdot}01$, this being a proportion which is often used in practice

$$k = \frac{0{\cdot}010a}{\frac{A}{B}}$$

From this equation and from the results given in the above table, the values for k are calculated in the table given on the next page.

The tables clearly show the interdependence of the various factors. By comparing, for example, experiments 8 and 16 or experiments 10 and 11, the influence of the coefficient $\frac{A}{B}$ can be seen, as these experiments are carried out with baths

Experiment	k	Experiment	k
1	0·230	10	0·220
2	0·229	11	0·217
3	0·225	12	0·217
4	0·224	13	0·213
5	0·225	14	0·207
6	0·225	15	0·208
7	0·226	16	0·203
8	0·220	17	0·196
9	0·221	18	0·109

of identical composition. The action is naturally the same as was discussed on page 172, when considering the influence of the proportion of cellulose to acid, which is, of course, proportional to the value $\frac{A}{B}$.

Example. The example given by Clément will show how his formula may be applied for calculating the required composition of the bath. The required nitrogen content n is 11 per cent. 1 kg. of paper, which would correspond to 1·54 kg. of cellulose nitrate, is to be treated with 100 kg. of acid and the proportion of sulphuric acid to nitric acid in the bath is to be 3/1. It should be noted that this proportion does not influence the degree of nitration, but merely the reaction velocity of the nitration process.

In this case, $A = 1{\cdot}54$, $B = 100$, and, therefore, $\frac{A}{B} = 0{\cdot}0154$. From the above tables we find that when $n = 11$, $k = 0{\cdot}217$. But as $a = \frac{k \cdot \frac{A}{B}}{0{\cdot}010}$ by inserting the above numerical values we find that

$$a = \frac{0{\cdot}217 \times 0{\cdot}0154}{0{\cdot}01} = 0{\cdot}334.$$

By inserting a, n and $\frac{A}{B}$ in the above equation for Z, we find

$$Z = \frac{46{\cdot}76 - 0{\cdot}2546 - 30{\cdot}49}{0{\cdot}76} = 21{\cdot}07$$

Thus, 21·07 per cent of water must be used, leaving 78·93 per cent for the sulphuric and nitric acids in the mixture. As these are present in the proportions of 3/1, we find 59·19 per cent H_2SO_4 and 19·74 per cent HNO_3.

The fact must, however, be emphasized, that this calculation is only of value if, during the nitration, all external influences, such as the absorption of moisture from the air, loss of nitric acid, etc., are eliminated, that is, if the nitration is carried out in a closed vessel ; otherwise these effects must be allowed for. (See also the article by Clément and Rivière on this matter, which extends the calculations to ordinary nitration practice, including change in weight of the nitration baths and the production cost of cellulose nitrate, in *Moniteur Scientifique*, 1912, p. 873 ; *Kunststoffe*, 1913, p. 203.)

Temperature and Duration of Nitration. The temperature of the nitration bath has no noticeable effect on the nitrogen contents of the product. An increase in the temperature greatly accelerates the nitration process, so that the maximum and optimum of nitration are attained in considerably shorter time. The duration of the nitration is therefore dependent on the temperature and must be determined for each temperature and definite composition of the bath by special experiment. If the nitration mixture is allowed to act on the cellulosic material for a longer period, decomposition takes place with saponification of the ester. Below 30° C. this decomposition is only slight, and is not noticeable at 0° C. even on standing for some days. Lunge and Weintraub (*Zts. f. angew. Chem.*, 1899, p. 448) carried out experiments on this subject by allowing nitration batches of identical composition to stand at various temperatures, investigating them all after half an hour. It was found that the maximum degree of nitration was attained within half an hour at 40° C., and that at 60° and 80° C. products were obtained with almost identical nitrogen contents. Further results showed, however, that this maximum was attained at 80° C. in a quarter of an hour only.

A high temperature acts on the nitration similarly to a

large excess of sulphuric acid (see page 173) by destroying the structure of the cellulosic material, so that even at a temperature of about 50° C. a short-fibred and brittle product is soon obtained.

Nitrogen Tetroxide. Any appreciable quantity of nitrogen tetroxide, N_2O_4, in the nitration bath, was formerly considered to be very detrimental, and Payen (*Comptes rendus*, Vol. 24, p. 86) considered that he had confirmed this view. Detailed investigations by Lunge and his pupils (*Zts.f.angew.Chem.*, 1899, p. 471) are in conflict with this opinion. No injurious effects could be detected with regard to the yield or stability of the nitrate, which was obtained either with highly concentrated acid mixtures or with mixtures containing 10 per cent of water, even though the proportion of N_2O_4 was more than 9 per cent, an amount which is certainly far higher than the maximum which could occur in practice. It was only when the proportion of tetroxide was increased to 12 per cent that a slight decrease in the nitrogen contents of the products could be observed. It may, therefore, be assumed that the nitrogen tetroxide contents of the nitration bath have absolutely no practical effect on the degree or character of the nitration.

Atmospheric Moisture. Finally, we may note that the atmospheric moisture may influence the nitration process appreciably. In very damp weather the nitration acid may absorb considerable quantities of water vapour ; but in this case, more particularly, the cotton which, as is well known, is very hygroscopic, absorbs considerable quantities of moisture, through the action of which the nitration bath is appreciably weakened. The atmospheric moisture, and more particularly the moisture contents of the cellulosic raw material, must be allowed for, and if necessary correspondingly stronger acids must be used.

The Practical Operation of the Nitration Process. Although in general, in the manufacture of collodium cotton for the artificial silk industry, the aim must be to obtain a cellulose nitrate containing as little nitrogen as possible and as completely soluble as possible in ether-alcohol, methyl alcohol, and so forth, a large number of variations of the process is

possible, as will be clear from the above theoretical and experimental data. Therefore, the methods of working adopted technically vary within fairly wide limits.

With regard to the proportion of cellulose to nitration acid, the weight of the latter is usually 25 to 30 times that of the cotton. Sometimes, however, proportions are used which are considerably greater or lower than these ; for example, according to the recipe of H. Wyss-Naef (*Zts. f. angew. Chem.*, 1899, p. 30) only 35 litres of nitration acid are used for 4 kg. of dry cotton. A considerably greater quantity of acid is also sometimes used. Clément (*Kunststoffe*, 1912, p. 384) recommends the proportion of 100 to 150 kg. of nitration acid to 1 kg. of paper for the manufacture of celluloid ; such proportions are presumably seldom employed. R. Müller (Ullmann, *Enzyklopädie der Technischen Chemie*, Vol. 3, p. 312) describes the use of 300 kg. of acid to 5 kg. of cotton ; that is, a weight relationship of 1/60. C. Piest assumes 50 to 60 parts of nitration acid to 1 part of dry cotton (Piest Stich, and Vieweg, *Das Celluloid*, 1913, p. 39). These quantities correspond to those employed by the old German process. In England a very large excess of nitration acid was formerly employed. Escales gives for the old English process (*Schiessbaumwolle*, 1905, p. 109) a proportion of about 176 kg. and for the old German process a proportion of 50 kg. of mixed acid per 1 kg. of cotton.

The variations in the processes used in different works with regard to composition of the nitration bath, temperature and duration of the nitration process, are still more considerable. C. Piest (*loc. cit.*, p. 36) gives a series of recipes which are reproduced in the following table—

	HNO_3 per cent	H_2SO_4 per cent	H_2O per cent	Temperature ° C.	Time hours
1	26·5	56·0	17·5	45	1
2	25·0	59·5	15·5	20	¾
3	40·0	40·0	20·0	45	1—2
4	19·96	63·92	16·12	40—42	2
5	19·64	62·02	18·38	40—42	2
6	20·00	61·04	18·96	40—42	1·6
7	20·42	62·08	17·50	45—46	1·4

The recipes 4 to 7 are due to W. Mitscherling (*Kunststoffe*, 1912, p. 261). He states that the best results are obtained with this composition of mixed acid. According to Guttmann (*Zts. f. angew. Chem.*, 1907, p. 262), it is usual in the manufacture of collodium cotton to nitrate at 40° C. with a mixture of equal parts of 75 per cent HNO_3 and 96 per cent H_2SO_4 for one to one and a half hours. The bath then contains about 37·5 per cent HNO_3, 48 per cent H_2SO_4 and 15 per cent H_2O. This mixture appears to be largely used. Guttmann states that the mixed acid recommended by Lunge, containing approximately equal proportions of nitric and sulphuric acid with 19 to 20 per cent of water, is too dear. Becker (*Die Kunstseide*, 1912, p. 109) states that a collodium cotton, especially suitable for artificial silk manufacture, is obtained by nitrating for 10 minutes at 50° C. with nitration acid containing 31·5 per cent HNO_3, 53·8 per cent H_2SO_4, and 14·7 per cent H_2O. This recipe, equally with the above recipe by Guttmann, may be assumed to be particularly suitable for the relatively weak collodium which is used in the wet spinning process (see below), whereas for the production of cellulose nitrate for the dry spinning process it is better to use dilute nitration mixtures containing about 19 per cent of water. According to Escales (*Schiessbaumwolle*, 1905, p. 153) the celluloid works use, for the manufacture of their collodium cotton, a mixture of 66 parts by weight of sulphuric acid, 17 parts by weight of nitric acid, and 17 to 20 parts by weight of water. This mixture is allowed to act on the cotton for 20 to 30 minutes at 30° C. Escales also gives other compositions of the nitration mixture. It is clear that there is no lack of recipes, and it may be said in this case with much justification that many methods lead to the same result.

The nitration process may be carried out in three different ways: nitration in pots or troughs, nitration in centrifuges, and finally, the continuous process, in continuous paper sheets. The latter process is, however, very seldom used. Each of these three processes offers advantages and disadvantages. A main advantage of the use of centrifuges is that the material is nitrated in an exceedingly uniform manner, and also that the

transference of the nitrocellulose into the centrifugal washers, whilst heavily laden with acid, which is usually necessary when nitrating in baths and is very obnoxious, expensive and dangerous, can be avoided. On the other hand, any required quantities of cellulose can be simultaneously nitrated in batteries of pots, according to the number and size of these, enabling nitration to be carried out for longer periods, for example, 2 hours. This is not possible when using centrifuges, as it would be too expensive to erect a large number of these. Therefore, when using the centrifugal system, short nitration periods are usually adopted—up to about half an hour. The process is also somewhat shortened by the fact that, as already mentioned, the operation of transferring the nitrocellulose heavily laden with acid from the pots into the centrifugal washers is avoided. Through the saving in time, therefore, the deficiency in available space is at any rate partially compensated. In any case, nitration centrifuges represent a relatively expensive plant, which also requires fairly frequent repairs, although the most modern types of centrifuges meet all requirements in a very satisfactory manner.

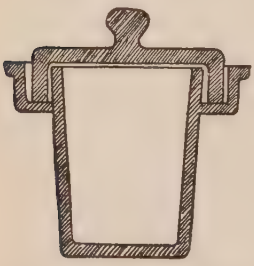


Fig. 74. Nitration Pot

Nitration in Pots or Troughs. The nitration pots which are used vary greatly in composition, shape, size and equipment. Porcelain or clay pots are usually preferred to iron pots, as traces of dissolved iron easily lead to a slightly yellow colour of the cellulose nitrate, which is to be avoided in the raw material, more especially for white silk, and which must otherwise be removed by special treatment (see below). The pots are usually bucket-shaped, as shown in Fig. 74.

Nitration pots of the simplest form are covered with a glass plate during nitration, this being perforated at one point so that the temperature of the batch can be measured by a thermometer. The pot shown in our illustration, which represents one of the most usual forms, is well sealed by means of a cover with a down-turned rim which fits into the double rim

of the pot. Some pots are fitted with a hood-shaped cover with a waste pipe for the vapours and gases. Some pots are also provided with a pipe socket for the introduction of acid, and with another below for removing the spent acid.

The pots are either placed in rows on the floor of the nitration house, or in water baths, or they are suspended in iron rings which are pivoted, so that they can readily and quickly be emptied by tipping ; otherwise the pots must be emptied by hand. In some pots, the excess of nitration acid can be withdrawn through a waste cock. The collodium cotton, soaked in acid, is withdrawn by means of large forks of iron or aluminium. The nitration pots are very often placed collectively in large numbers, as batteries, in water baths. These latter are flat iron basins in which water is circulated, the temperature of which can be controlled according to the required nitration temperature, and which can be cooled or heated for that purpose. Such temperature regulation can, however, be dispensed with by warming the nitration acid to an empirically determined temperature, some degrees below the required temperature of nitration. On introducing the cellulose, the temperature usually rises slightly above the required nitration temperature, but soon falls to this point and remains practically constant throughout the whole nitration.

The size of nitration pots varies greatly. Formerly, small pots of 10 to 15 litres capacity were almost always used. They are also very practical for the production of highly nitrated products, or when high nitration temperatures are employed. For the production of collodium cotton for artificial silk, and in all cases when relatively low nitrated products are to be produced, as also in the case of celluloid, and in which the nitration temperature should not exceed 40° C. at the highest, the nitration can safely be carried out in larger batches. For these purposes, therefore, it is found that pots of less than 30 to 50 litres capacity are seldom used, but that far larger pots, up to about 300 litres capacity, are met with. Charges of $\frac{1}{2}$ kg. to about 5 kg. are used, according to the size of pot. In a battery of 20 large pots carrying charges of about 5 kg.

each, 750 kg. of cotton can be nitrated in 24 hours with a production of almost 1000 kg. of cellulose nitrate.

Earthenware hoods are employed above the pots assembled in the form of batteries, through which the evolved acid vapours are withdrawn by means of fans. Pots which are provided with a pipe for the withdrawal of the acid vapours are united by means of these to a common exit main situated above the series of pots. In these pots, the cover is usually divided ; the front half can be removed whilst the waste gas tube is attached to the remote half.

The pots are frequently provided with a false bottom, on which the cotton or nitrocellulose lies. The pipe socket for removing the acid is, of course, fitted below this false bottom.

Large troughs are sometimes used instead of the pots, consisting of rectangular cast iron containers which may, for example, be 2 m. to 3 m. long, 80 cm. high, and 60 cm. broad. They are usually divided by partitions into several separate compartments—usually 4 to 6. These troughs may also conveniently be placed in larger containers, in which cooling water circulates.

The nitration is carried out by first filling the pots or troughs with the nitration acid which has been warmed to the prescribed temperature. A workman then slowly throws the accurately weighed charge of cellulose into the pot in small portions. It is immediately submerged by a second workman by means of a rod or fork of iron or aluminium. The temperature must be carefully controlled so that no overheating may occur. Towards the end of the dipping process, the mixture in the pot forms a fairly compact mass, so that the introduction and dipping of the final portions of the cellulose require considerable exertion.

Thomson's Process. A somewhat more complicated method of pot nitration is described by Thomson. (See Lunge ; *Zts. f. d. ges. Schiess- und Sprengstoffwesen*, 1905, p. 2 ; and also *Zts. f. angew Chem.*, 1906, p. 151.) The peculiarity of this process is, more particularly, that after nitration is completed, the nitration acid is displaced by slowly-added water, which forms a layer above the heavier acid mixture. Before adding the water, a perforated aluminium sheet is placed over the collodium cotton, which is supported on a similar sheet ; by this means admixture of the water with the acid is largely prevented. It is

stated that by this process annoyance through acid vapours is completely avoided.

Piest (*loc. cit.*, p. 44) states that highly-nitrated cellulose can be satisfactorily produced by this method, but that collodium cotton can only be manufactured under definite conditions. If, for example, the water contents of the mixture are high and at the same time nitration is carried out at a somewhat higher temperature, for example, at about 50° C., decomposition and fuming-off easily occurs on displacing the mixed acid by water. It is stated that by this process nitric acid is recovered in fairly concentrated form and with a high yield.

Macdonald (*Zts. f. d. ges. Schiess- und Sprengstoffwesen*, 1911, p. 389) states that by the Thomson process the loss of acid amounts to 0·1 kg. per kg. of cellulose nitrate, whilst with the nitration centrifuge it amounts to 1·0 kg., being 10 times as great. The process has, however, great disadvantages. The cellulose is unevenly nitrated, particularly if it contains a little grease or moisture; fuming-off is said to be extremely frequent, particularly in the summer, and interruptions in manufacture are said to occur very frequently, and many repairs are said to be necessary. (See, for example, Delphy, *Zts. f. d. ges. Schiess- und Sprengstoffwesen*, 1912, p. 237.) Moreover, much time is required for the displacement of the acid.

By the Thomson apparatus, one charge is stated to require 6 to 8 hours, including nitration, replacement of the acid and washing. In the nitration centrifuge, on the other hand, the whole operation requires 1 to $1\frac{1}{2}$ hours only. In spite of many advantages, the process has, therefore, been but little introduced in practice, mainly in England, and is now probably scarcely used anywhere.

During the nitration, samples are removed from time to time in order to test the condition of the fibre. Very frequently it is tested by examination under polarized light, its behaviour with regard to which alters during the nitration. The end of the nitration process is indicated by a steel blue colour and uniform appearance of all the fibres between crossed Nicols.

After completion of the nitration, that is, after the prescribed nitration period is completed, the cellulose nitrate must be separated from the acid and completely freed from the same by washing. The removal of the charge is carried out by various methods. In some works, the nitration pots are conveyed on low trucks to the special shed in which the acid centrifuges are placed, and the whole of the contents are emptied directly into the hydro-extractors and centrifuged. In other works, the pots are emptied in the nitration shed into larger tanks containing a sieve plate and mounted on trucks, from which the acid is removed and in which the cellulose nitrate, which is

still soaked with acid, is conveyed to the centrifuges and hydro-extracted ; or the spent acid is withdrawn directly from the nitration pots, which are provided with one or more cocks for the purpose. In these cases, the cellulose nitrate is frequently allowed to stand for some time in the pots, or in larger containers, after the main portion of the acid has been withdrawn, and before it is brought into contact with water ; during this period it cools off and undergoes a useful after-nitration. During this process cold water is usually passed through the water tanks in which the pots stand or in which they are placed for the purpose. The nitrated cotton is frequently freed from the adherent spent acid by squeezing it with a fork, or by a special lever attached to the wall for the purpose, on to a grid situated above the nitration pot. The first washing of the nitrate is also frequently carried out in the nitration pots or vats. For this purpose a water-cock and hose are provided above each pot or vat, with the help of which the cellulose nitrate is soaked in water, after nitration is completed and the spent acid has been withdrawn. After being washed for some time in this manner, it is conveyed to the washing tanks, in which the washing is completed, and is finally dried in the centrifuges.

It should be noted that the most dangerous stage of the whole process occurs when the cellulose nitrate has just been freed from the main quantity of spent acid, because the capillaries of the fibres are still largely filled with acid, which may give rise to sudden decomposition. Therefore, for example, when nitrating in a centrifuge, fuming-off most frequently occurs at this stage, for the above or other causes.

Regarding the acid centrifuges in which the cellulose nitrate is freed from the adherent remaining acid, the remarks apply which are made below when dealing with nitration centrifuges. Centrifuges are also constructed which can be used for either purpose. In these acid centrifuges, as in the others, earthenware fittings or linings for all parts which come into contact with the acid are preferred.

Nitration centrifuges were first used in 1893, in the explosive works at Troisdorf ; they are constructed in an absolutely

similar manner to ordinary centrifuges, with the difference that they also serve as dipping vessels, being so arranged that the acid which is introduced is not immediately withdrawn, but that this only occurs on opening one or more valves, which operation may be effected automatically when the centrifuge commences to rotate. Such centrifuges are also provided with flues (through which the acid vapours are withdrawn by means of powerful fans, which are preferably constructed of stoneware). In order to increase the uniformity of the nitration, centrifuges are often used with continuous circulation of nitration acid. Centrifuges of this type are constructed, for example, by Selwig & Lange, of Brunswick. The acid is circulated through the cellulose charge by rotating the drum during nitration at a relatively slow speed. Nitration centrifuges were originally built of iron, but, as in the pot nitration processes, it was soon found that the collodium cotton assumed a yellow colour through the effect of dissolved iron, and that this colour was not always easily removed. According to Piest (*loc. cit.*, p. 41) this difficulty can be avoided, even with iron centrifuges, if these are so constructed that the nitration acid comes into contact with steel and wrought iron only, but not with cast iron. Centrifuges have also been constructed, the inner container and cage of which are formed of aluminium. According to Piest (*loc. cit.*) aluminium is, however, too strongly attacked by the nitration acid. The most suitable centrifuges from this standpoint are those which either have stoneware cages or are completely lined with stoneware. A nitration centrifuge of the most modern type, constructed by C. G. Haubold, A.-G., Chemnitz, is shown in Fig. 75.

In principle, the system of working with the nitration centrifuge is similar to pot nitration until nitration is completed. The container is filled with mixed acid to the height of the cage or to the edge of the drum, and the cellulose charge is added by hand in small portions and dipped with a rod or a fork. There are also centrifuges in which dipping occurs automatically on slowly revolving the drum, by means of a flap which dips obliquely into the acid. The nitration usually lasts about half an hour.

After nitration is completed, the discharge cock is opened and the charge is centrifuged. The centrifuge may then be emptied in a similar manner to that adopted when pots or tanks are used. Satisfactory results have also been obtained

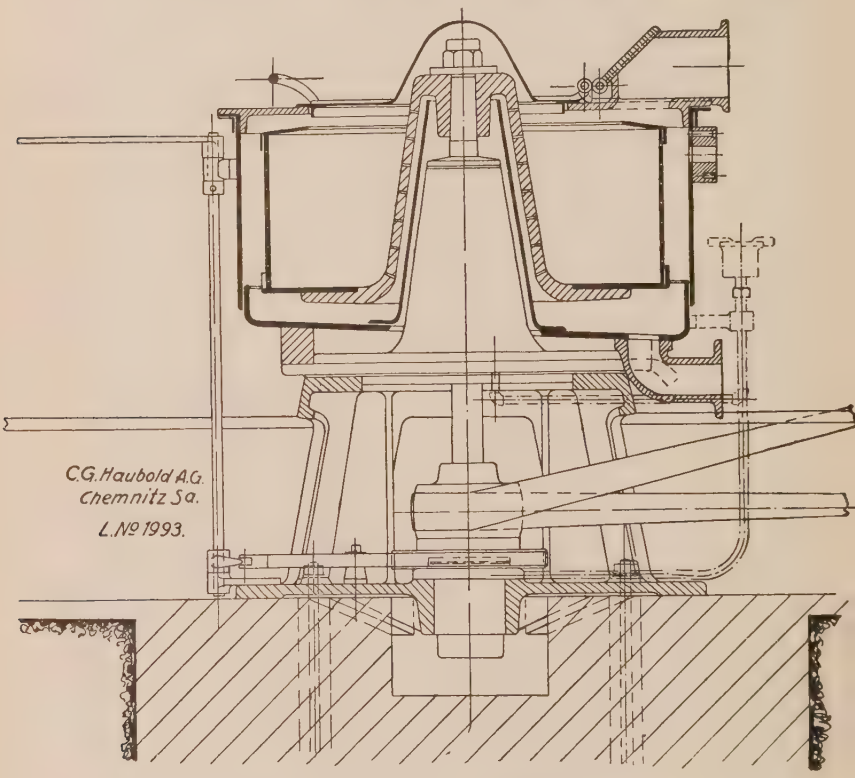


Fig. 75. Nitration Centrifuge

by the removal of the nitrated charge by a flushing apparatus, such, for example, as is described in German patent 107,923 of Selwig & Lange, Brunswick. According to this patent, a stoneware funnel, covered by a wide hood with lateral opening, is attached by an elbow tube to a flushing main about 25 cm. wide. The hood is connected with a fan to remove the nitration gases. The nitrated charge is removed from the centrifuge with tongs, thrown through the lateral opening of the hood,

carried away by the water which falls down the funnel on all sides, and conveyed to the locality where it is further treated, by the water passing down the attached flushing main, if necessary with the help of an interposed centrifugal pump.

If the actual nitration takes half an hour, the total cycle of operations requires 50 to 55 minutes, so that 11 to 12 charges can be treated in each centrifuge in 10 hours. The sizes of centrifuges vary ; for example, Escales (*Schiessbaumwolle*, 1905, p. 103) describes two usual sizes, the diameters of the drums being 850 mm. in the one case, and 1000 mm. in the other ; the respective heights of the drums are 360 mm. and 380 mm. 6·5 kg. to 8 kg. of cotton can be nitrated in the smaller centrifuge, and 10 kg. to 12 kg. in the larger, so that the daily output of the smaller drum is about 125 kg. of cellulose nitrate and about 185 kg. in the larger.

Nitration in continuous sheet form, which is but little used, requires great care and attention ; in this process, the cellulose is passed continuously through the nitration bath in the form of a continuous sheet of paper. The rate of passage through the bath is naturally very low. The composition and temperature of the bath are so arranged that the duration of the nitration process shall be as short as possible. The subsequent operations can also be arranged to be carried out simultaneously. In German patent 59,929, a process is described in which the paper is calendered, nitrated, washed, dried and re-wound in one single machine. It is obvious that the manufacturing difficulties of such a continuous process are by no means small.

Washing the Cellulose Nitrate. The collodium cotton produced and washed free from the bulk of the spent acid by one or other of the above described processes, has to be completely freed from acid by a thorough washing operation. In some of the above-mentioned methods of working the first washing follows directly after nitration, either by introducing water into the nitrating pot or vat, or by flushing the product out of the centrifuge. According to other methods of operation, the nitrated material is carried to washing vats directly after treatment by the centrifuges. Such washing vats usually consist of large wooden vats or cement-lined tanks which are

sometimes lined with wood. The collodium cotton is first thoroughly washed with cold water, which is frequently renewed or preferably by a continuous stream of fresh water. Washing is continued until the wash water no longer turns blue litmus paper red.

Special machinery has also been constructed which effects especially intensive washing of the cellulose nitrate. Plant of this type includes the so-called kneading machines of Carl Krafft & Söhne, Düren ; the tangential washing machines of the Vereinigten Tonwarenwerke ; and finally, the washing apparatus operated by compressed air, described in U.S. patent 743,932 (1903) of F. J. du Pont, Wilmington, Del., U.S.A.

The stabilization of the nitrated cotton after cold washing consists in careful boiling with water or direct steam and is not nearly so important in the case of collodium cotton for artificial silk as for cellulose nitrate, which is to be converted into celluloid or blasting gelatin, as collodium silk is in any case subsequently denitrated, whilst the durability of the other products is dependent on very careful stabilization. The purpose of stabilization is the removal of the last trace of acid adhering to the collodium cotton and the destruction of certain unstable compounds which are relatively easily decomposed and which are formed in very small amounts as nitration by-products, and may give rise to gradual or sudden decomposition processes. These products are probably mainly nitrated degradation products of cellulose, such as nitrates of dextrin and sugar derivatives. Nitrated xylane (wood gum) is said to be also present according to Piest (*loc. cit.*, p. 53), but its presence is very doubtful. The small quantities of wood gum which the cotton may contain are presumably completely removed by the pre-treatment. (See the description, page 61, *et seq.*)

For purposes of artificial silk manufacture it is sufficient, after washing the nitration product in the cold, to wash thoroughly with hot water, and then to disintegrate it to about 1 mm. length of fibre in a pulp engine. This process usually requires not more than 6 to 8 hours, and opens out the capillaries more completely, so that the washing liquid can penetrate

into the interior of the fibres, after which the product is again boiled once or twice with water, and then thoroughly washed. Pulp mills used for the purpose are preferably fitted with bronze knives rather than with iron knives, as the latter are strongly attacked by even minute traces of acid. The addition of alkaline reagents, such as lime, to neutralize the acid, is less to be recommended. According to German patent 150,319 (1902) of Selwig & Lange, stabilization is effected by steaming in special steam centrifuges. According to German patent 348,136 of the Elektro-Osmose, A.-G., cellulose nitrate may be very satisfactorily stabilized by the electro-osmotic displacement process, and they state that this can be effected more quickly than by the ordinary stabilization processes.

The washing process, and particularly the treatment with hot water or steam, not only purifies the product, but also causes changes in the collodium cotton itself, although to a relatively small degree. The amount of this change depends on the intensity of the treatment and more particularly of the hot treatment. According to Piest (*loc. cit.*, p. 53), the viscosity of the solutions obtained from the cellulose nitrate is reduced by the washing process, and by repeated washings at the boil the nitrogen content is somewhat lowered and the solubility increased.

Bleaching. It is not always necessary to bleach the finished collodium cotton, especially if its colour is pure and bright, and if the material is required for coloured silk. The yellow colour caused by traces of iron can be removed during washing by the addition of hydrochloric acid, which must in turn be thoroughly removed, or by a little bleach liquor. In cases, however, in which it is desirable to bleach the collodium cotton, more particularly if this is intended for the production of white silk, this is conveniently carried out after boiling ; that is, immediately before the final washing. A solution of potassium permanganate of 0·01 to 0·02 per cent concentration, acidified with sulphuric acid (0·03 per cent H_2SO_4) was formerly frequently used for bleaching the product. 3 to 4 gm. of permanganate and 8 to 10 gm. of concentrated sulphuric acid were required per kilogram of cellulose. To-day, bleaching

with electrolytic bleaching liquor (sodium hypochlorite) is generally preferred to the permanganate bleach. Details will be found in an earlier chapter.

After bleaching, the product must naturally once more be thoroughly washed. The finally washed product is again centrifuged, undergoes a preliminary drying if necessary, and is then fully dried in large drying chambers or vacuum driers. The drying temperature must, of course, not be too high. Usually a current of warm air at 40° to 45° C. is passed through the drying chambers, and removes the water vapour. Vacuum driers are frequently used, and are provided with a double-walled jacket and superposed heating plates, through which warm water at the same temperature circulates.

It is, however, not always necessary to dry the collodium cotton completely, as this is sometimes dissolved in the presence of considerable quantities of water, as we will see later.

Yield. When the process is suitably carried out, about 150 kg. of collodium cotton are obtained from 100 kg. of cotton. The quantities of chemicals used are about 140 kg. of nitric acid of 85 to 90 per cent concentration ; 100 kg. of 70 per cent sulphuric acid and 2 kg. of 96 per cent sulphuric acid (see Piest, *loc. cit.*, p. 43).

Regeneration of Acid. The spent acid can be utilized in two ways. It can either be revivified, that is, strengthened to the original composition by the addition of acid, and used for further nitrations, or it may be denitrated, that is, the nitric acid is separated from the sulphuric acid and each acid used separately, generally for other manufactures.

The first process, the regeneration process, and direct re-utilization, is limited by the accumulation in the spent acid of organic matter derived from the cellulosic raw material, which gradually increases the contamination of the acid. In a report by G. W. Patterson on the English process (see Escales, *loc. cit.*, p. 110), it is stated that the spent acid can apparently be regenerated indefinitely as long as it never contains more than 5·5 per cent of nitrogen oxides ; but it should be remembered that according to the English process nitration is carried out with an exceptionally large excess of acid, which therefore

takes up a very small percentage of organic matter at each nitration, and can consequently undergo a correspondingly far greater number of regeneration processes, which circumstances may have led to the view expressed. It is also to be noted that according to this process compressed air is frequently blown into the acid for hours, for the purpose of effecting thorough mixing. It is possible that this would lead to the oxidation of the less stable organic compounds. According to Guttmann (see Escales, *loc. cit.*, p. 167), the spent acid must frequently be regenerated before it is denitrated (about ten times in some works), in order to produce a cellulose nitrate at as cheap a cost as possible. It is, however, necessary to start with but little water, in order that the ten-fold regeneration may not lead to difficulties.

With regard to the method of working such regeneration processes, the only correct method is, of course, to analyse the spent acid, after thorough mixing in the large tanks in which it is stored, to calculate the required quantities of acids to be added on the basis of the analysis, and to mix them thoroughly with the spent acid after their addition. It is, however, quite wrong to regenerate according to an empirical formula without any analytical control, as was usual in many works ; that is, to rely mainly on the addition of a definite proportion of fresh acid in every case.

Chardonnet already carried out a method of denitrification of the spent acid, in order to recover nitric acid and sulphuric acid, and described it in German patent 56,655. According to this process, the spent acid is first introduced into a still which is heated to about 170° C., from which a portion of the nitric acid is distilled in a fairly pure condition. The residue, which contains the whole of the sulphuric acid and a portion of the nitric acid, is passed through a leaden tube into a second still, in which the remainder of the nitric acid is distilled at a temperature of about 200° to 210° C.

The so-called denitrifiers, which are much used, are cast iron towers lined with acid-proof bricks, which are filled with pumice or other filling bodies. The spent acid trickles down the tower from above, whilst superheated steam and air are

injected below. At a temperature of 150° to 160° C. nitric acid is driven off and escapes to the top of the tower, from where it is carried to a battery of absorption vessels, whilst the sulphuric acid is discharged at the bottom free from nitric acid. The recovered nitric acid is of about 40 to 50 per cent concentration, and the sulphuric acid of about 60 to 70 per cent. Both acids, particularly the sulphuric acid, are rather impure, and dark yellow to brown in colour, and are usually sold for other industrial purposes, such as the manufacture of fertilizers, and so forth. It is stated that purer and much more concentrated acids, which can be directly re-utilized, can be obtained in the denitrifiers constructed by Evers. The principle which he uses is the same as that of the above described plant, but by intensive admixture of the acid with the injected air and steam at temperatures of about 175° C., complete combustion of the organic substances is effected (see Escales, *loc. cit.*, p. 112).

According to German patent 299,680 of S. Hamburger, the nitration acid is recovered by washing with sulphuric acid of such a concentration that its water contents correspond approximately to those of the nitration acid.

Collodium Cotton. Nitrated cellulose, whether collodium cotton or gun-cotton, is of exactly the same fibrous structure as the raw material. The characteristic twists in the fibre which characterize cotton vanish during nitration. The fibre untwists, and appears under the microscope as a smooth, ribbon-like structure. The surface is harder and rougher, and the soft feel of the raw material consequently vanishes. On compression a slightly rustling effect can be observed.

De Mosenthal (*Journal Soc. Chem. Ind.*, 1907, p. 443), found the specific gravity of various cellulose nitrates to be almost exactly equal, the average being 1·66.

The *refractive index* decreases as the proportion of nitrogen increases. De Mosenthal found that whilst the refractive index of pure cotton cellulose was 1·531, that of the lower cellulose nitrates was 1·514, and of the more highly nitrated products 1·5091.

Solutions of cellulose nitrate in ether-alcohol or acetone turn

the plane of polarized light to the right. Constant values have, however, apparently not been obtained. Vignon (*Bull Soc. Chim.*, 1904, p. 105), found $[\alpha]_D = +19 - 21°$.

In polarized light highly nitrated cellulose is readily distinguished from ordinary cellulose by its blue colour, the un-nitrated product showing a yellow to brownish-yellow colour. It is, however, not possible sharply to distinguish the various stages of nitration by this means. It is only possible to distinguish weak and strong degrees of nitration within fairly wide limits (see Lunge and Bebie, *Zts. f. angew. Chem.*, 1901, p. 566, *et seq.*). According to De Mosenthal, cellulose nitrates of the same stage of nitration, but which have been prepared from different raw material, or by different methods, show different colours in polarized light.

The *hygroscopicity* of cellulose nitrates is much smaller than that of pure cellulose, the difference being usually the greater the higher the nitrogen content. Beadle (*Chemical News*, Vol. 70, p. 247) was probably the first to call attention to the relations between hygroscopicity and nitrogen contents. Will (*Mitt. Zentralst. Neubabelsberg*, p. 15) has shown that the sum of the nitrogen contents and the hygroscopicity is constant, and has an average value of 14·6. This sum remains constant regardless of the raw material or of variations of pre-treatment, nitration, after-treatment and so forth. It is also independent of the surface of the material, and therefore remains unaltered, for example, if it is reprecipitated, say, from acetone solution.

The less stable nitrates possess a higher degree of hygroscopicity. The hygroscopicity is greatly dependent on the temperature, and becomes smaller as the temperature rises.

Cellulose nitrates quite commonly contain considerable quantities of unattacked cellulose ; this is, of course, a fundamental fault, and must more particularly be avoided in the case of collodium cotton for the manufacture of artificial silk, as it interferes with the necessary complete solubility.

The ash content of cellulose nitrates is normally very small, and about 0·1 to 0·2 per cent. It may, however, amount to 2 per cent and more, especially if the raw material is impure. According to Hake and Bell (*Journal Soc. Chem. Ind.*, 1909,

p. 460), cellulose nitrates always contain some sulphur, probably in the form of cellulose sulphuric esters, or of the mixed nitric and sulphuric esters, already referred to.

The ignition temperature of the explosive cellulose nitrates is about 180° C., should never be appreciably lower than 160° C., and is ordinarily tested at 150° C. The composition of the nitration acid influences the velocity of decomposition of cellulose nitrates greatly, this being a function of the nitrogen contents.

Cellulose nitrates decompose more or less slowly, even at the ordinary temperature. Their stability depends essentially on the degree of purity. Under certain circumstances decomposition occurs extraordinarily slowly, so that the products may be considered as practically absolutely stable. Escales states (*loc. cit.*, p. 7) that samples of cellulose nitrates still exist, at the Bernoullianum in Basle, which date from the year 1846, and were prepared by Schönbein and the gunsmith Sauerbrey. According to Will, however (*Ber. d. Chem. Ges.*, 1904, p. 291), these samples are decomposed and have partially been replaced by others. However, Will himself (*loc. cit.*, p. 290) has examined samples of cellulose nitrate from the Dynamit—A.-G. vorm. Alfred Nobel & Co., which were more than 40 years old, and portions of which, at any rate, were still of the best quality. Stability is an important factor in cellulose nitrates intended for the manufacture of gun-cotton or blasting gelatine, but is of no particular importance for the collodium silk industry, as the nitrates are denitrated after spinning.

Acids saponify cellulose nitrates. The form in which the cellulose is liberated depends on the character and concentration of the acid, the temperature of reaction and so forth. According to Carlson (*Ber. d. chem. Ges.*, 1907, pp. 4191–4194), the whole of the cellulose was recovered on acidification in the form of a fine powder, from cellulose nitrate containing 12·5 per cent of nitrogen. Chardonnet recommended dilute nitric acid for the denitration of artificial silk, that is, for saponifying the nitrate without damaging the cellulose fibre. (See German patents 46,125 and 56,655.) This procedure will be considered later. Compare also the information on page 168, regarding the

equilibrium in the nitration mixture in consequence of the saponifying action of the acids.

Caustic alkalis, earth alkalis and alkali carbonates also saponify the cellulose nitrate molecules, but simultaneously cause a more fundamental decomposition of the cellulose complex, so that the cellulose is in this case not regenerated as such (see Häussermann, *Chem. Ztg.*, 1905, p. 421). According to Eder (*Ber. d. chem. Ges.*, 1880, p. 184) and Berl and Smith (*J. Soc. Chem. Ind.*, 1908, p. 537) it appears, however, that by the gentle action of alkali it is possible to saponify partially, in the first instance, to form lower nitrates ; this is, however, disputed by Will (*Ber. d. chem. Ges.*, 1891, p. 401).

The saponification of cellulose nitrates can be carried out easily and with the least possible alteration of the cellulose complex, by means of certain salts, more particularly of reducing salts, hydrosulphides and sulphides. Solutions of these salts are, therefore, used in collodium silk manufacture for denitrating the artificial silk fibres, and we will therefore consider the action of these in detail later, when discussing the denitration process, page 212, *et seq.*

Reducing Action. If cellulose nitrates are tested in the usual manner with Fehling solution, it is found that this is considerably reduced. Vignon (*Bull. Soc. Chim.*, 1898, p. 858) found by quantitative determinations that the reducing activity is independent of the degree of nitration. He found, for example, that with weakly nitrated material containing 8·19 per cent of nitrogen he obtained the same amount of reduction as with highly nitrated cellulose containing 13·9 per cent of nitrogen. It should be noted, however, that Fehling solution is strongly alkaline, and we have already seen that alkalis not only saponify cellulose nitrates, but also degrade the cellulose complex, presumably assisted by the action of the nitric acid residues. It is to be expected that reducing substances should thus be produced, as was already pointed out by Schwalbe (*Chemie der Cellulose*, p. 297). From the property of reducing Fehling solution no definite conclusion can therefore be drawn with regard to the constitution of the cellulose nitrate molecule or of any particular groups which it may contain.

The action of iodine and sulphuric acid or of a solution of iodine in potassium iodide, merely colours cellulose nitrate to a more or less weak brown tint, and this coloration disappears on washing with water. It disappears more easily on washing as the degree of nitration of the cellulose increases (see Lunge and Bebie, *Zts. f. angew Chem.*, 1901, p. 567). We may remind the reader that unaltered cellulose assumes a deep blue colour with these reagents (see page 20).

The behaviour of the more or less highly nitrated cellulose nitrates towards dyestuffs, and also of the denitrated artificial silk obtained from these (which is of more particular interest to us) is very different from that of pure cellulose. Details regarding these differences will be given in the section on the dyeing of artificial silk.

Behaviour Towards Solvents. We have already mentioned (page 166) that the various cellulose nitrates differ greatly in their behaviour towards solvents, but that for the manufacture of artificial silk the readily soluble collodium cottons are alone used ; for it is possible to spin a clear solution only in a satisfactory manner. Further details on the behaviour towards solvents will be given in the next section on the production of collodium.

PRODUCTION OF COLLODIUM

Solvents. There are a large number of solvents for cellulose nitrates, some of which are chemically pure liquids, others mixtures of liquids, whilst finally, others are solutions of solid substances in liquid media. The behaviour of the various cellulose nitrates with the individual solvents varies very greatly, and not all solvents are available for all nitrates. Cellulose nitrates of the same degree of nitration may vary greatly in solubility. Berl and Klaye (*Zts. f. d. ges. Schiess- u. Sprengst.*, 1907, p. 381) assume these differences to be due to varying molecular magnitudes of the nitrate molecules. In the case of one and the same product solubility is usually considerably dependent on the moisture content and also on the temperature at which solution occurs. Statements in the literature regarding the various solvents are often contradictory. In one

place one may find a statement that cellulose nitrates are insoluble in a particular liquid which is elsewhere described as a suitable solvent. These contradictions may be explained by the varying behaviour of cellulose nitrates towards solvents already referred to, as the various authors were evidently dealing with nitrates of different quality, or carried out the solution under different conditions, for example, with materials containing different quantities of moisture. It has already been mentioned that quite generally the highly nitrated gun-cottons containing more than 12 to 12·5 per cent of nitrogen are less soluble than the lower nitrates.

Bronnert and Schlumberger, in their German patent 93,009 of 1895, and British patent 6858/1896, already mentioned the following as well-known solvents for cellulose nitrates : acetic acid, alone or mixed with alcohol or ether ; sulphuric acid ; ethyl sulphuric acid ; aldehydes ; aniline ; solutions of camphor in alcohol, ether, benzene, toluene or carbon tetrachloride ; ethyl-acetate ; acetone ; ether-alcohol ; wood spirit (methyl-alcohol) ; nitro-glycerine ; nitro-benzene and amyl acetate.

According to German patent 52,977, Du Vivier proposes to replace the ether-alcohol mixture used by Chardonnet by glacial acetic acid. According to German patent 55,949, Lehner dissolves cellulose nitrate in wood spirit alone, whereas in German patent 58,508, he proposes the use of a mixture of wood spirit or ether (3 parts) with ethyl sulphuric acid (1 part). He dissolves 8 parts of cellulose nitrate in 100 parts of this mixture by warming to 30° C. for one hour. R. Valette (in French patent 344,660, and English patent 20,637/1904) refers to the use of equal parts of ether and alcohol, which he proposes to replace by a mixture of equal parts of acetone and methyl- or ethyl-alcohol, to which he may add glacial acetic acid. According to French patent 344,845, Turgard dissolves cellulose nitrate in a mixture of 4 parts of alcohol and 1 part of glacial acetic acid to an approximately 33 per cent solution. According to French patents 346,693 and 350,723, Cazeneuve uses acetone alone, as does also Germain, according to French patent 360,395 ; whereas in French patent 354,424, Gorrand proposes a mixture of acetone, amyl-alcohol, and ethyl-acetate (in the corresponding English patent he mentions acetic anhydride instead of ethyl-acetate). He states that a little acetic acid should also be added to the solution.

According to the statements of J. Duquesnoy in German patent 135,316, a solution of cellulose nitrate in acetone, alone or with the addition of acetic acid, leaves on evaporation of the solvent a white, opaque, crumbly mass, whilst a suitable material is obtained if amyl-alcohol is used together with acetone and acetic acid. He emphasizes the advantage of using a mixture of these three components, whereas he states that amyl-alcohol, either alone or in admixture with acetone or acetic acid only, does not give suitable results. He adds, however,

that good threads can be obtained from a solution of acetone or ethyl-acetate only, if the action of moisture is avoided during the formation of the fibre either from the spinning solution or from the air. A whole series of patents (for example, German patent 210,867, French patents 368,190, 373,947, 386,107, and 401,343) therefore recommend the use of dried air or direct heat during the formation and winding of the fibre.

A collodium of complicated composition is described by A. Cadoret in *L'Industrie Textile*, 1896, p. 227. He dissolves 50 kg. of cellulose nitrate in a mixture of 0·8 kg. glacial acetic acid, 9·2 kg. ether, 18·4 kg. acetone, 6·6 kg. alcohol and 3·0 kg. toluene, with small further additions of non-solvents. In this manner, however, he merely obtains a kind of paste, which is treated by heated rollers similarly to celluloid, by which means 20 to 25 per cent of the solvents which were used are recovered.

In French patent 383,555, Huwart recommends as solvents for cellulose nitrates the symmetrical and unsymmetrical acetals of the aliphatic series and their chlorine, bromine, aldehydic and ether derivatives, and also mixtures of these substances, such as, for example, a solution of methylal in 3 to 4 parts of ethyl-alcohol.

In British patent 3139/1911, German patent 246,651, Austrian patent 53,099, and French patent 425,900, A. Wohl recommends formic acid esters as cellulose nitrate solvents, and in the British and French patents, methyl-acetate in addition. In German patent 343,162, Weiler-ter-Meer proposes a mixture of paraldehyde and alcohol as a solvent. According to A. Dryen's German patent 339,011, cellulose nitrate is dissolved in acetone or ethyl-acetate and alcohol, more particularly for wet spinning in dilute sulphuric acid.

In German patent 93,009 of 1895, of Bronnert and Schlumberger (which has already been referred to) the use of alcoholic salt solutions was proposed as solvents for cellulose nitrates. The following salts are mentioned as examples: ammonium chloride, calcium chloride, magnesium chloride, aluminium chloride, zinc chloride, sodium lactate, potassium acetate and ammonium acetate. In spite of the fact that it contains too low a proportion of cellulose nitrate, the collodium prepared in the cold with the help of these salt solutions is very viscous. If, however, solution is carried out with warming, the cellulose complex is more or less attacked by the above-mentioned salts with hydrolytic dissociation. This was probably the cause of the failure, already discussed in the Historical Chapter, page 7, of Lehner, at Glattbrugg, when he carried out experiments by this process.

The same principle is found in Sauverzac's French patent 402,950, according to which alcoholic solutions of metallic chlorides are used as solvents for cellulose nitrate; for example, a solution of 10 gm. of aluminium chloride in 100 cc. of alcohol is said to dissolve 50 gm. of cellulose nitrate. It appears to be impossible that a fluid spinning solution should be produced with such a high percentage of cellulose nitrate; either there is an error in the figures, or the patentee is really concerned with a paste, and not a fluid spinning solution. The solution may be diluted with known solvents of cellulose nitrate, and it is said to be possible to incorporate 80 per cent or more of water, by which

means the fibre is said to become very elastic and soft. This also appears to be a very doubtful procedure, and actually the process was of no practical importance.

Very few of the above-mentioned solvents are actually used in technical practice. Methyl- and ethyl-alcohol and ether, usually admixed, are still the main solvents used. A mixture of ether and alcohol was, from the commencement, the most commonly used solvent for cellulose nitrate for all manner of purposes, in the form of collodium. The proportions of the two components of the solvent, alcohol and ether, may vary within wide limits, and either the ether or the alcohol may be present in excess. Lunge and Bebie (*Zts. f. angew Chem.*, 1901, p. 537) have studied these conditions more closely. Their essential results are embodied in the following table—

Parts of alcohol	Parts of ether	Solubility
1	6	Complete
1	9	Less soluble
1	12	92·1 per cent solubility
3	1	Complete
6	1	Less soluble
12	1	Almost complete
24	1	95·6 per cent solubility

Thus we see that the proportion of ether can be much more greatly reduced than that of the alcohol, so that the latter appears to be the more important constituent of the solvent. This agrees with the fact that absolute alcohol alone is a better solvent than ether alone, but it also depends on the process of spinning. In its original form the dry spinning process requires a larger proportion of easily volatile solvent, that is, more ether, than the wet spinning process.

A large excess of ether is used according to R. Lumière's process, described in German patent 171,752. This is mainly for the purpose of obtaining a solution which is easily filtered, from which about one-half the quantity of ether is removed by distillation after filtration. 300 kg. of dry cellulose nitrate are dissolved in a mixture of 1600 litres of ether, 200 litres of

methyl-alcohol, and 200 litres of ethyl-alcohol ; after filtration about 1000 litres of ether are distilled off, so that the collodium still contains 3 parts of ether to 1 part of ethyl-alcohol and 1 part of methyl-alcohol.

Chardonnet uses various proportions in his ether-alcohol mixture. In German patents 38,368 and 56,331, he refers to 40 per cent of ether and 60 per cent of alcohol ; he first dissolves pyroxylin in a mixture of equal parts of ether and alcohol and then adds the remainder of the alcohol. In German patent 81,599 and French patent 231,230, he recommends the reverse proportions, namely, 40 per cent of alcohol and 60 per cent of ether.

W. Mitscherling (*Kunststoffe*, 1912, p. 264) mentions the following as a mixture which has proved satisfactory in practice: 94 per cent methyl-alcohol, 2 per cent ethyl-alcohol and 4 per cent ether ; or 94 per cent methyl-alcohol, 4 per cent ethyl-alcohol and 2 per cent ether. This mixture is, however, only suitable for the wet spinning process. In the case of exceptionally highly nitrated collodium cotton he adds rather more ether, but never more than 10 per cent ; or he uses methyl-alcohol and ether only. He considers that ethyl-alcohol increases the strength of the fibre, whilst ether easily makes it hard.

As already mentioned, the water contents of cellulose nitrate have a certain influence on its solubility. Chardonnet, according to German patent 81,599, and British patent 24,638/1893, had already found that pyroxyline containing water was more easily soluble in ether-alcohol than the dry product. He therefore ceased drying his cellulose nitrate when it still contained 25 to 30 per cent of water. In this condition he states that its solubility exceeds that of the dry product by 25 to 30 per cent. He states that this product has a different appearance under the microscope in polarized light than the dry product, and that he could not obtain it from the latter by moistening, and he therefore assumed that it was a hydrate of cellulose nitrate. According to J. Stoerk (British patent 26,982 1902, German patent 169,931, Austrian patent 25,031, French patent 327,301) a cellulose nitrate containing less than 12 per cent of

water is not sufficiently soluble in ether-alcohol, whilst a product containing more than 27 per cent of water yields poor, turbid, dull and brittle fibres by the dry spinning process. He states that the optimum amount of water is between 12 and 20 per cent. We doubt, however, if this statement is quite general. Presumably, the conditions depend greatly on the quality of the cellulose nitrate, on the relative proportions of ether and alcohol, and so forth. It is, therefore, not surprising that other inventors give other figures for the optimum water contents: for example, Lacroix (British patent 2192/1905, Austrian patent 26,486, French patent 351,265) gives 35 to 45 per cent; von Dietl (British patent 15,029/1905, French patent 356,323), 33 to 38 per cent; and Kunstfädengesellschaft m.b.H. Jülich (British patent 27,527/1906, U.S. patent 866,766, French patent 371,544), 20 to 25 per cent. In their German patent 273,936 (which will be discussed later), Berl and Isler recommend the use of collodium prepared from cellulose nitrate containing 20 to 30 per cent of water.

Generally, however, in spite of its many advantages, moist cellulose nitrate is no longer used, and is replaced by absolutely dry material.

Additions to the Collodium Solution. Formerly hundreds of additions were recommended, but are scarcely used to-day. They were intended for the most various purposes.

Chardonnet recommended the addition of a reducing metallic chloride (ferrous, chromous, manganous or stannous chloride) and of oxidizable organic bases, or alkaloids, the purpose of which was the reduction of explosibility of the spun collodium. In order to increase the solubility of the collodium cotton and the fluidity of the collodium, he recommended, in the additional patent to his French patent 231,230, small amounts (a few hundredths of a per cent) of methyl-chloride, ethyl-chloride, magnesium, aluminium, manganous or stannous chloride, acetic acid, aldehydes, carbon disulphide; hydrochloric, nitric or sulphuric acid. The last-mentioned addition of small amounts of acids is probably the only one which is still occasionally used if it is desired to render the collodium solution rather more fluid. According to Dulitz (*Chem. Ztg.*, 1910, p. 991), such an addition of acid has the disadvantage that the formation of oxy-cellulose is promoted during the denitration process. Apart from this it is, of course, also necessary to provide for the presence of acid in the solution in the construction of the apparatus. In British patents 2694/1887, and 2695/1887, and German patent 40,373, Gérard proposes to add traces of calcium chloride to a solution

of collodium cotton in glacial acetic acid, in order to render the product incombustible. In order to increase the flexibility of the product, he recommends the addition of gluten, glucose, honey, glycerine, castor oil, linseed oil containing manganese, fats or gum lac. According to German patent 82,555 of F. Lehner, he mixes with the cellulose nitrate, moistened with acid (before it is dissolved in methyl-alcohol, acetone or ethyl-alcohol), a vulcanized drying oil, the preparation of which is described in detail in the patent. The purpose was " as far as possible to maintain the readily movable nitro-compound in the mixture at the same stage of nitration, and during the later deoxidation to admix with the nitro-groups an unchangeable compound which should act as a cement or skeleton between the molecules on resinification, and thus hinder too great a disintegration."

According to British patent 2476/1902, Austrian patent 21,118, U.S. patent 699,155, and French patent 315,543, J. Douge recommends the addition to the cellulose nitrate dissolved in ethyl-alcohol, of aqueous alkali, such as potash, soda, ammonia, alkali carbonate, lime, baryta, sodium borate, alkali silicate, and so forth. His object is to neutralize the acid which is formed on evaporating the solvent.

L. Crespin dissolves cellulose nitrate in a mixture of methyl-alcohol, ethyl-alcohol and ether, with the addition of castor oil, palm oil, or glycerine. (See British patent 27,565/1904, U.S. patent 820,351, Swiss patents 32,540 and 32,541, French patent 342,077. Vittenet dissolves pyroxylin in acetone, through which he has previously passed sulphur dioxide, but the amount of the acid may vary between a few thousandths and 30 per cent. The purpose is to avoid the precipitation of a pyroxyline-acetone compound unsuitable for the production of artificial silk, and the fibre which he produces is said to be more durable than one obtained with ether-alcohol. (See British patent 89/05, German patent 171,639, Austrian patent 24,849, French patent 350,383, and addition 5491, and U.S. patent 842,125.)

A. Dubosc (*Bull Soc. Ind. de Rouen*, 1908, p. 471) proposes to avoid denitration by adding to the collodium solutions salts which evolve incombustible gases on heating. As such he mentions ammonium chloride; double chlorides of ammonium and metals; ammonium borates and double borates of zinc and ammonium; ammonium phosphates and double phosphates; ammonium zincates and double zincates; ammonium sulpho-zincates and ammonium chloro-zincates. The double chloride of ammonium and zinc is said to be especially active. P. Germain attempts to obtain the same result in French patent 360,396, by the addition of ammonium phosphate, ammonium bicarbonate, magnesium bicarbonate, and similar salts; and Plaisetty (British patent 9087/1900), by the addition of aluminium salts, which are also proposed for the same purpose in French patent 328,054.

A. Petit (British patent 15,343/1900, Swiss patent 22,503, U.S. patent 665,975) adds to 100 parts of dry cellulose nitrate dissolved in ether-alcohol, 7 parts of rubber solution and 5 parts of stannous chloride, or of another tin salt. The threads are said to be rendered insensitive to water by the rubber solution, and flammable with difficulty by the tin salt, so that denitration becomes unnecessary. The same

additions are recommended by La Grange in Swiss patent 22,680. The suggested effects would, no doubt, be achieved, at any rate to a certain extent, but the fibres would be useless in other respects.

In German patent 338,495, Hildesheimer proposes the use of glycol esters of the fatty acids of non-drying oils, as additions for the purpose of keeping the fibre flexible.

According to Dulitz, all additions such as resins, oils, oleic acid, and so forth, interfere greatly with uniform denitration, even when well mixed with the collodium, as they offer resistance to the penetration of the denitrating agent between the smallest particles of cellulose nitrate. He states that when using additions of any kind to the collodium he never obtained such a good and strong thread as when no such addition was made. This view is in agreement with the method of working which is now general, in which additions of any kind are avoided as far as possible. If necessary, a very small amount of acid is added to the collodium if the mass is too thick and viscous ; even in this case care is necessary. According to Dulitz, such an addition of acid is dangerous on account of the tendency to form oxy-cellulose on denitration.

THE SPINNING OF COLLODIUM SILK

The general principles of the spinning process, the phenomena by which it is accompanied, and the most important parts of the spinning machine have already been discussed in the section of the previous chapters dealing with these matters.

Whereas both cuprammonium silk and viscose silk are usually spun wet, that is, by means of spinning baths, in the case of collodium silk both a wet spinning and a dry spinning process are used ; in the latter process no spinning bath is required, but the spinning solution is discharged directly into the air, leaving a solid thread of cellulose nitrate through the evaporation of the solvent. We will find that similar conditions occur in the case of acetate silk, and it appears that latterly more attention has been paid to the dry spinning of other silks.

The Wet Spinning Process. This process was originally used by Chardonnet and described in his first patents. (See, for example, German patents 38,368 and 56,331). He caused the warm collodium solution to pass through a mouthpiece dipping

into cold water, by which means the thin, discharged stream of fluid immediately solidified at its surface and formed a solid filament. The filament, which consisted at first of an outer solid capillary containing liquid collodium solution internally, was stretched after leaving the bath, during which process the whole of the thread became solid. According to Chardonnet, the pressure at which the collodium solution was expelled from the nozzles was 10 to 12 atmospheres. (See, for example, German patent 56,331). This pressure was obtained by forcing air into the container holding the collodium by means of an air compressor. After Chardonnet had discovered the dry spinning process, and had found that " any collodium containing more than 15 to 20 per cent of nitrocellulose immediately formed a filament on being discharged from the nozzle aperture, without coming into contact with water," he still recommended spinning the thread with the use of water in order " to obtain an artificial silk fibre with the necessary properties." For this purpose the thread was caused, for example, to enter a suspended drop of water or to pass with friction against a strongly-wetted surface. (See French patent 231,230 of 30th June, 1893.) Du Vivier also spun his acetic acid collodium, already referred to, in water by the wet spinning process, but he added alkalis in order to neutralize the acetic acid and passed the thread through further baths, namely : a 3 per cent albumen bath " in order to endow the thread with animal properties " ; a coagulating bath of carbolic acid or mercuric chloride and a bath of an aluminium salt in order to reduce the inflammability ; occasionally a further albumen bath followed in order to smoothen the surface. (See German patent 52,977.) It was stated that this series of baths could be replaced by the following three baths: a 5 per cent sodium bisulphite solution, a 0·3 per cent albumen solution, and finally a coagulating bath consisting of 0·3 per cent carbolic acid solution. The sodium bisulphite bath was stated to offer the further advantage that it had a bleaching action. The article already referred to, marketed under the name of *Soie de France*, was produced according to this process.

A special apparatus for the manufacture of collodium silk by the wet spinning process, using water, is described in Swiss patent 4449, of the firm of E. Mertz, Basle, which built Chardonnet's first machine. In British patent 27,565/1904, French patent 342,077, Swiss patents 32,540 and 32,541, and U.S. patent 820,351, L. Crespin proposed to discharge the collodium solution from fine openings into the bottom of a cylinder through which water was passed. The water flowed upwards, at a speed which could be regulated, and carried the thread up the cylinder. At the upper end of the cylinder the water could be withdrawn, together with the solvent which it had absorbed, whilst the thread ran on and was wound.

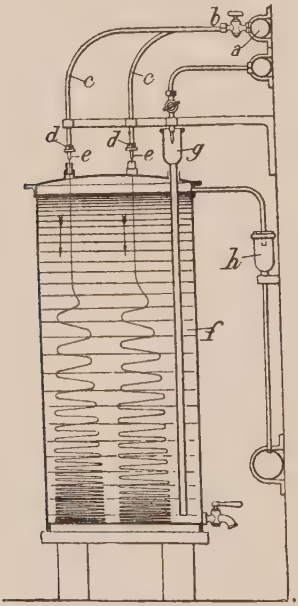
A whole number of other liquids have been proposed as coagulants instead of water. F. Lehner also worked by the dry spinning process, but ordinarily used and developed the wet spinning process. He refers to the following coagulants in his German patent 58,508 : turpentine, juniper oil, petroleum, benzine, benzene, liquid hydrocarbons and chloroform. In French patent 344,845, Turgard recommends a 1 per cent alum solution as a coagulant. According to British patent 14,216/1914, German patent 273,936, Dutch patent 2089, U.S. patent 1,188,718, and French patent 473,446, Berl and Isler precipitate a collodium which is produced in the usual manner from cellulose nitrate, containing 20 to 30 per cent of water, by aqueous alcohol containing 20 to 50 per cent of alcohol by volume at a temperature not exceeding the boiling point of ether. According to German patent 177,957 of the firm of A. Lumière, a precipitating agent is used consisting of a solvent for cellulose nitrate to which such quantities of other liquids are added that the solvent is just deprived of its capacity for dissolving that substance ; as an example, methyl-alcohol, containing 5 to 8 per cent of water, is mentioned.

Fig. 76 shows the apparatus used for the purpose. The precipitation bath is contained in the tank *f*, and is constantly maintained in motion by being introduced through the pipe *g*, and discharged through the pipe *h*. The spinning solution (collodium) is introduced through the inlet pipe *a*, the cock *b*, the tubes *c*, and the nozzles *d* and *e*. As the precipitating liquid is of low specific gravity, the threads which are formed sink immediately. The process can at best only be used for thick single threads (artificial horse-hair).

According to French patent 420,086, Sauverzac proposes to use a mixture of water, alcohol and a chloride, such as aluminium or sodium chloride, or an organic chloride such as carbon tetrachloride " for the recovery of the alcohol and ether." Apparently the collodium is to be spun in these liquids. In British patent 89/1907, German patent 200,265/1906, French patent 382,718, Swiss patent 38,910, and U.S. patent 888,260, A. Lumière describes a process in which the collodium thread discharged from the spinning nozzle, before reaching the spinning

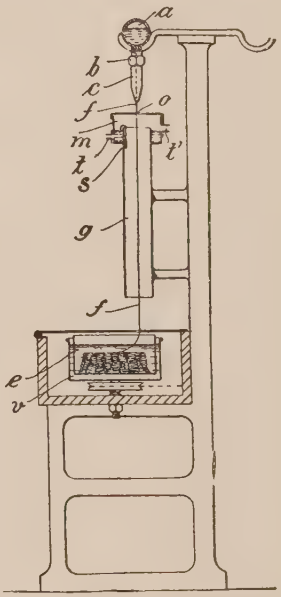
bath, passes vertically through a tube of considerable length in which concentrated alcohol is evaporated, in order to prevent premature drying and consequent shrinking of the thread. If the collodium solution and spinning bath are of the right composition such a measure is unnecessary.

Apparatus for carrying out the process is shown in Fig. 77. The spinning nozzle *c* is attached to the supply tube *a* by the screw-connection *b*. The thread *f* discharged from the nozzle passes through the



(*Soc. A. Lumière*)

FIG. 76. APPARATUS FOR SOLVENT RECOVERY
(German patent 177,957)



(*Soc. A. Lumière*)

FIG. 77. APPARATUS FOR SOLVENT RECOVERY
(German patent 200,265)

aperture *o*, in the cover, into the cylinder *g*, and through this into the spinning bath, which is contained in the vessel *e*, placed in the larger container *v*. The cylinder *g* is lined inside with an absorptive fabric which is constantly moistened with alcohol contained in the channel *m*, which is in turn supplied through *t*. The excess of alcohol is discharged through the opening t^1. The container *v* is maintained in constant motion during spinning by means of the underlying cord and pulley, so that the thread is deposited in regular coils, which can readily be removed. This process, in conjunction with the earlier one described by the same firm, is presumably mainly used for the production of artificial horse-hair.

In German patent 339,011, A. Dryen recommends the use of sulphuric

acid as a spinning bath, more particularly of solutions containing 30 to 75 per cent of H_2SO_4.

To-day, in the manufacture of collodium silk, the wet spinning process in water has probably been entirely replaced by the dry spinning process, although the recovery of the solvents, in particular, is simpler and more certain by the former process, and the coagulation of the thread is not dependent on the very varying composition of the atmosphere, as is the case in the latter process. When methyl-alcohol is the main solvent for the cellulose nitrate its recovery in the wet spinning process is particularly effective, as it is easily and completely dissolved by water. According to Mitscherling, it is advantageous to spin, not into pure water, but into water containing a definite proportion of methyl-alcohol, by which means a distinctly better thread is said to be obtained. A further advantage of the wet spinning process is due to the fact that relatively very small pressures are required and that the apparatus can be constructed in a correspondingly light and inexpensive form. As fibres, when first formed, may be relatively thick and may be stretched before complete solidification, as was already done by Lehner (German patent 58,508/1890, Swiss patent 3740), much wider spinning apertures may be used, up to about 0·5 mm. diameter, and a pressure suffices such that the spinning solution is just extruded. In the apparatus described in the patent by Lehner, which has just been mentioned, the pressure is produced by a difference of level of the two liquids amounting to a few centimetres only. However, the wet spinning process does not permit of the rapid rate of withdrawal which can be employed with the more concentrated spinning solutions used in the dry spinning process, and the output is correspondingly smaller. Lehner endeavoured to convert the spinning process into a continuous process by combining spinning, twisting, denitrating, and reeling into a single operation. (See Swiss patent 4984.) The threads were impregnated with a denitration liquid immediately after production, and were then twisted and further treated, alone or together with other textile fibres. In technical practice it was, however, found impossible to carry out the process in this form.

The Dry Spinning Process. Certain disadvantages of the dry spinning process have already been mentioned in previous pages, namely the more difficult recovery of the solvents and dependence on the varying conditions of the atmospheric air; also the fact that in this process very much higher pressures, up to 50 atmospheres, are required for both filtration and spinning, on account of the high concentration of the spinning solution; therefore a correspondingly massive apparatus is necessary. High concentration of the spinning solution is, however, necessary in order to achieve as rapid as possible a solidification of the fibre in the air. On the other hand, however, certain advantages are gained which are not to be despised; as the concentrated collodium can be much more rapidly drawn out to a thread, the output per nozzle and per unit of time is considerably greater than in the wet spinning process. Considerable economies of solvent are, of course, possible, as in consequence of the high concentration less is required for a given weight of cellulose nitrate; yet the solution requires a relatively large amount of volatile solvent in order to solidify rapidly in the air, and, more particularly, much relatively expensive ether. It will be seen that the disadvantages and advantages of the wet and dry spinning processes almost balance. In practice the simpler apparatus, smaller quantities of solvents and larger output appear to favour the dry spinning process, which is now probably used in most collodium silk works. However, local conditions, such as the prices of ether and alcohol, and other considerations, play a part in this matter, and, therefore, the wets pinning process is still preferred in some places.

Apart from the heavier construction necessitated by the high pressures, the spinning apparatus used for the dry spinning process is simpler than for the wet spinning process. The arrangements have already been described in detail in an earlier chapter, pages 76 and 84. As the individual filaments have to be discharged from the nozzles in a very thin form, in order to solidify rapidly in the air, very small nozzle apertures are used in the dry spinning process, usually of about 0·07 to 0·1 mm. diameter. Any considerable stretching

of the threads, as used in the wet spinning process, is usually out of the question in this case.

The dry spinning process was first mentioned by Chardonnet in his German patent 81,599/1893, when he found that his solution of pyroxylin hydrate, containing 25 to 30 per cent of water, already referred to, immediately solidified, without contact with water, on expelling it into the air from fine capillaries, and formed a fibre which did not adhere to neighbouring fibres, as it became absolutely hard "in the course of a few hundredths of a second." Meanwhile, views on the correct method of operating the dry spinning process varied greatly. In his above-mentioned British patent 26,982/1902, German patent 169,931/1902, French patent 327,301, and Austrian patent 25,031, J. Stoerk states the dry spinning process can only be satisfactorily carried out and supply a satisfactory fibre if the water contents of the cellulose nitrate which is used are between 12 and 20 per cent. On the other hand, the Droogenbosch Company state in their British patent 5076/1901 (Austrian patent 6947) that dry cellulose nitrate can be more advantageously spun than wet. This contradiction obviously arises from the fact that the water contents of the pyroxylin are by no means the decisive factor in working the dry spinning process, but that the character of the cellulose nitrate itself, the composition and concentration of the solvent and the spinning solution, temperature and moisture of the atmosphere, and so forth, all have an appreciable influence. We have already met with similar contradictory statements regarding the composition of the spinning solution. Moreover, in his French patent 231,230 of 1893, Chardonnet already mentioned the fact that any collodium containing more than 15 to 20 per cent of cellulose nitrate immediately formed a thread without contact with water on discharge from the spinning aperture. F. Lehner originally carried out his dry spinning process according to German patent 55,949, by discharging collodium solution from a fine aperture freely on to a smooth, revolving hollow cylinder, and simultaneously evaporating the solvent by heat. Boullier also treated his collodium, containing acetone or ethyl-acetate as a solvent, by the dry spinning process. In British patent 16,512/1907 and French patent 368,190, he states that this collodium only yields good fibres if the vapour tension of the solvent is so increased that it is as near as possible to that of ether-alcohol, which result may be attained by raising the temperature to 30° to 35° C., by the addition of ether or other low-boiling compounds, also by spinning in air, which is as dry as possible, or by using several of these methods. Somewhat more complicated dry spinning machines are described in Loewe's German patent 234,927 and in Denis's German patent 277,154, and French patent 473,481.

AFTER-TREATMENT OF COLLODIUM SILK

The silk is now treated as previously described; that is, it is first re-wound, twisted and reeled, and is then submitted to the denitration process in hank form.

Denitration. From the beginning it was quite evident that the ready inflammability of the cellulose nitrate thread was a very serious obstacle to its use as a textile material, which must, therefore, necessarily be removed or very much reduced. There were two possibilities: one could either lessen inflammability by admixture with suitable substances, or one could saponify the cellulose nitrate, that is, split off nitric acid or denitrate the product, and reconvert the thread into cellulose or cellulose hydrate. The latter method appeared to be the safer, and Chardonnet soon discovered a satisfactory denitration process. The other method was, however, attempted, more particularly as denitration had certain very definite disadvantages; it was difficult to carry out, it removed or reduced valuable properties of the fibre, peculiar to cellulose nitrate, such as strength, resistance to water, lustre and so forth, and also greatly reduced the output. A large number of additions to the spinning solution were therefore suggested with the object of reducing the great inflammability of the material. We already discussed these additions when considering the spinning solution, page 203, *et seq.* To-day, such methods have become obsolete, and the denitration process is exclusively used.

The process is very simple in principle, and consists essentially in hanging the hanks of artificial silk in the denitration bath for a definite time, removing them after denitration is complete, and washing them thoroughly. The practical operation of the denitration process is, however, difficult, and has to be carried out with much special knowledge and care. The denitration baths appreciably attack the regenerated cellulose hydrate, probably mainly through the oxidizing action of the ONO_2 group detached from the cellulose nitrate, and the fibre is thus weakened. Dulitz found that if the denitration process is badly carried out considerable quantities of cellulose dissolve in the denitration liquor, presumably in the form of oxycellulose, through the influence of the ammonia which is simultaneously produced. The silk should therefore not remain in the denitration bath for longer than is absolutely necessary. On the other hand, denitration must not be too

incomplete and the finished silk should not contain more than about 0·05 per cent of nitrogen. It is, therefore, of importance to obtain as complete a denitration as possible with the least possible weakening of the fibre. It is also, of course, important that the lustre of the fibre should not be impaired. Further, the process must be carried out with complete uniformity, for irregularly denitrated material leads to uneven dyeing. This uniformity must not merely apply to the hanks dyed in one and the same bath, but also to large deliveries. It is clear that the smallest mistake may spoil large quantities of artificial silk, for damage undergone during this process is usually irreparable and the material cannot be utilized, whereas, for example, a badly nitrated cellulose can mostly be used for other purposes.

A. Dulitz (*Chem. Ztg.*, 1900, page 990) mentions the following requirements for the denitration process : " (1) A uniform nitrocellulose thread of absolutely constant nitrogen contents, produced with even shrinkage and duration of shrinkage ; (2) uniform water contents of the threads submitted to the denitration liquor ; (3) a constant quantity of denitration liquor per kilogram of nitrocellulose ; (4) constant composition of the denitration baths ; (5) constant initial temperature of these ; (6) uniform warming or cooling of the liquors during the process ; and (7) uniform duration of the action of the denitration liquid on the fibres." Dulitz adds that the denitration must also be cheap, and that care must be taken that the nitric acid liberated during the process should be rapidly converted into nitrate, which oxidizes the cellulose to a comparatively slight extent.

The following conditions for satisfactory denitration, which are similar, are given by W. Mitscherling (*Kunststoffe*, 1912, page 309): " (*a*) Care must be taken during spinning that the thread is uniform and during nitration that the nitrogen contents of the nitrocellulose are constant ; (*b*) the water contents must be maintained constant within narrow limits ; (*c*) during nitration a definite quantity of the bath per kilogram of silk must be used ; (*d*) the composition of the denitration bath must be constant ; (*e*) the initial and final

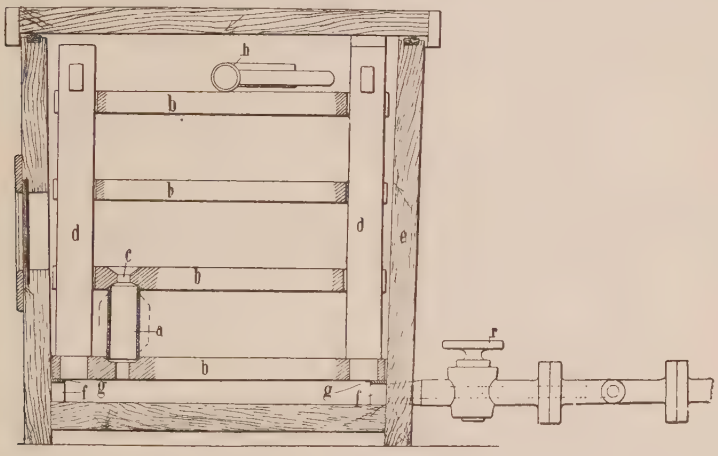
temperatures must be maintained constant; (*f*) the duration of the action of the denitration liquor on the fibre must be maintained constant."

Denitrating Agents. The most important of these are reducing sulphur compounds, some of which were already used by Chardonnet (see German patent 56,655, French patent 221,488, and addition to the latter patent of the year 1893), such as calcium, ammonium and sodium hydrosulphides, which are still used, probably without exception, in all works; additions of various kinds are used with these materials, but are usually kept secret by the various works; sulphides are also used.

Chardonnet first used for denitration 50 per cent nitric acid at 32° to 35° C., but achieved only partial denitration and obtained a product with 6 to 6½ per cent of nitrogen. In German patent 56,655/1890, he recommends as newer denitration agents, by which he claims to remove the nitric acid completely, concentrated solutions of sulphides, polysulphides or sulphocarbonates of the alkalis, alkaline earths or earth metals. In German patent 125,392/1901, and in the patents of addition 139,442 and 139,899, A. Richter mentions as suitable denitration agents, solutions of metallic salts which are readily converted into salts of a higher degree of oxidation. He states that cuprous chloride and cuprous oxychloride are particularly active, but that solutions of various manganous, chromous, antimonious, stannous, mercurous and cobaltous salts give good results. These salts are stated to be active both in acid and in alkaline solution, and also in the presence of alkali chlorides only. According to O. Knöfler (British patent 11,038/1895, German patent 88,556, and U.S. patent 593,106), aqueous denitrating baths are unsuitable for the production of collodium silk for the manufacture of incandescent gas mantles, as they dissolve the inorganic salts associated with the fibre. For this particular purpose he therefore proposes that denitration should be carried out by the use of formaldehyde, hydroxylamine or similar reducing agents, which may suitably be added to the organic liquids used as fixing agents, such as benzine, benzene and so forth.

The Denitration Process. The silk is most conveniently

denitrated in the form of loose hanks, as the liquid can then penetrate to all parts of the thread much more quickly and more uniformly than if the material were wound on bobbins. This is, therefore, the usual method of working, and the threads have usually already been doubled. The Compagnie de la Soie de Beaulieu considers that the penetration of the denitration bath into doubled threads is more difficult, and



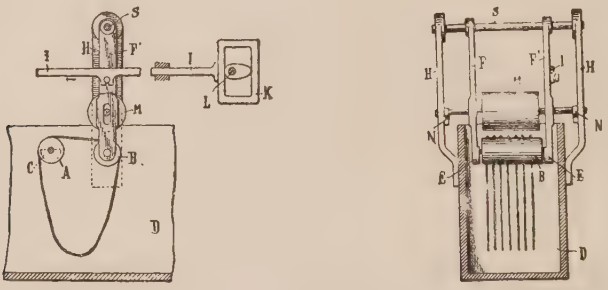
(*Cie de la Soie de Beaulieu*)

FIG. 78. DENITRATION FRAME

obtained patent protection for carrying out denitration with untwisted threads (British patent 17,460/1907, German patent 217,128, Austrian patent 42,740, and French patent 378,143).

According to these patents denitration is carried out on perforated bobbins in the container *e* shown in Fig. 78. The bobbins *a* are placed on the stand constructed of beams *d* and plates *b*, in which they are held between india-rubber cushions *g*. The container can be closed by means of a cover, and is then evacuated, after which the denitration liquor is allowed to enter. This penetrates the bobbins and the silk with which these are covered, from within to without, and on emptying traverses the thread once more from without to within. The process is cumbrous, and the effects did not realize expectations.

Denitration is carried out similarly to hank dyeing, in large wooden or stoneware vats in hank form. The hanks are suspended from smooth rods of hard wood or from glass stirrups which are bent to hooks at either end. The hanks are turned over these rods exactly as in ordinary dyeing. Details of the exact method of turning are given by Mitscherling (*loc. cit.*). The baths are heated by steam coils, and the temperature should preferably not exceed 40° C. As heat is liberated by the denitration process and the bath therefore becomes warmer



(*Bernstein*)

FIGS. 79A AND 79B. AUTOMATIC DENITRATION MACHINE

spontaneously, the hanks are preferably introduced into the solution at a lower temperature of 20° to 25° C.

In German patent 232,373, A. Bernstein describes an apparatus by which manual labour can be dispensed with during denitration; this would offer the double advantage of saving the thread from damage and avoiding the action of noxious gases on the workpeople. The apparatus, which is shown in Figs. 79A and 79B, consists mainly of a roller *A* on a fixed bearing, and a movable pair of rollers *B* and *M*, which are carried in a rocker *F* turning about a point *S*, and so arranged that during the motion of the rocker in one direction the rollers which it carries grip the hank and carry it over the fixed roller, whilst when moving in the other direction they release their grip. The axle of the fixed roller is directly attached to the wall of the vat *D*, whilst the rocker is attached to the vat by the support *H*. The rocker is actuated by the crank-rod *I*, which is rigidly attached to the frame *K* within which an eccentric revolves, which is actuated by the shaft *L*.

The period of denitration is naturally dependent on the character of the thread and method of working, on the nature of the denitrating agent, the temperature, and so forth. When

using sulphocarbonates, for example, Chardonnet recommends treatment for 12 hours at 35° C., or for 36 hours in the cold. When using ammonium hydrosulphide, he recommends " digestion for 12 or 24 hours, at 60° or 70° C." With modern processes using calcium or sodium hydrosulphide a much shorter time is required, which amounts on the average to 2 or 3 hours, according to the temperature, and sometimes even less, say $1\frac{1}{2}$ hours.

For the reasons already mentioned, it is necessary to control the denitration exactly and to interrupt the process at the right moment, a matter requiring much experience and practice. The end of the operation is recognized by various methods in various works. An experienced operator can approximately recognize the end of the operation by the appearance and feel of the silk. The exact determination of the completion of the operation, so far as possible, is now usually carried out by titration of the denitration bath with iodine solution and by the investigation of samples of the thread in the polarizing microscope. Neither method possesses the exactitude of a quantitative analysis, but both require empirical adjustment. When titrating with iodine solution preliminary experiments are carried out with the material used in order to determine the reduction of the sulphide radical in the denitration bath by determining the quantity of this radical present before and after the denitration. The denitration is then always considered to be finished, when the same amount of hydrogen sulphide has disappeared. (See also details on page 212, *et seq.*). Complete uniformity of the material to be denitrated, and very exact working, are required. Even so, mistakes may occur owing to the fact that varying amounts of hydrogen sulphide escape into the atmosphere according to the weather conditions. The determination of the end point with the polarizing microscope is even more difficult and more uncertain, and requires a carefully-schooled eye. The blue colour of the cellulose nitrate thread is replaced by the rainbow colours of pure cellulose. In many works, both methods of testing are employed simultaneously, so that the one can be more or less controlled by the other ; but even so, all uncertainty is not avoided, and in order to be quite certain it is

usually necessary to leave the silk in the denitration bath for a few minutes beyond the time at which denitration has apparently ended, whereby, however, as already explained, the continued action of the denitrating bath may prejudicially affect the strength of the fibre.

Additions to the Denitration Bath. We have already mentioned that most additions made to the collodium solution, more particularly resins, oils, and fatty materials, which remain in the thread, exercise an unfavourable influence on the denitration process. (See page 205.)

In the denitration bath, also, all unnecessary additions should be avoided as they usually interfere with the completion and uniformity of denitration. The only usual addition is that of a base in order to fix the liberated nitric acid and of a reagent for accelerating the reaction. The only bases which can be used are those which unite with the nitric acid to form a nitrate with as little oxidizing action as possible on cellulose. The nature of such additions is kept strictly secret by the various works. In order to start and to accelerate the reaction, the remains of the nitric acid added to the collodium solution can be used ; these are frequently only partially removed in order that they may be available for this purpose. In order to avoid the production of spots occasionally caused by the separation of sulphur, H. D. Turgard (U.S. patent 508,124 and French patent 218,759), proposes to use ammonium hydrosulphide together with a metallic sulphide soluble in a solution of the former, such as, for example, silver sulphide, and to introduce the cellulose nitrate threads into such a solution at a temperature not exceeding 20° C.

The denitrated silk is first thoroughly washed with water : it then usually has a dirty, greenish-grey colour, mainly due to the presence of iron sulphide ; this can be removed by treatment with hot, very dilute hydrochloric acid, after which the fibre is once more washed.

Bleaching and dyeing then follow, and are both carried out in the manner already described. We wish particularly to refer to the remarks in the section on collodium silk in particular. (See pages 152 and 153.)

If the feel of the silk is too hard it can be much improved by after-treatment with soap solution, for which purpose it is sufficient to pass the hanks several times through a warm, 0·5 to 1 per cent, solution of Marseilles soap, followed by thorough washing. It is still better to add the soap to the bleach liquor, as already described.

On the further treatment of the fibre see page 160, and on the dyeing of collodium silk see page 345.

Recovery of Solvents. Owing to the relatively high cost of the solvents used for dissolving collodium, their recovery is of great importance, and may be of decisive effect on the profits of any particular process; therefore, ways and means of carrying out this recovery have been sought for since the commencement of the technical production of collodium silk, and the number of patents dealing with this matter is extremely large, so that we can only mention the more important.

According to German patent 56,331, and Swiss patent 1958, Chardonnet carried out the recovery by passing the hot air escaping from the spinning machine slowly through three condensing pots which were cooled with water; the first of these contained potassium carbonate solution and the two others concentrated sulphuric acid. His later improvements will be referred to below. Barbet et Fils use dilute sulphuric acid, according to French patent 101,723. In British patent 4534/1905, German patent 165,331, Swiss patent 33,571, U.S. patent 834,460, and French patent 341,173, Denis describes an apparatus in which the precipitation liquid, namely water, is heated to a temperature higher than the boiling point of ether, and constantly circulates within a closed system. The spinning nozzles open into tubes which belong to this closed system. The ether evaporates immediately, whilst the alcohol is absorbed by the water. The ether vapours are aspirated and led to a condensing plant. As soon as the circulating precipitating liquor is strongly enriched with alcohol the greater portion of it is removed and replaced by water, whilst alcohol is distilled from the abstracted portion. The doubtful feature of the process appears to be the rapid removal of the ether, which may cause distortion, formation of bubbles, and so forth in the thread. In German patent 267,509, and Belgian patent 248,315, the same inventor describes a fairly complicated arrangement, in which the solvents are recovered during continuous circulation in pipe systems which are completely closed from the point of exit to the point of re-entry into the system, and in which the mixture of air and vapours is led through refrigerating baths. According to Dervin (French patent 350,298), the alcohol and ether vapours in the air withdrawn from the spinning machine are recovered by absorption in strong sulphuric acid of about 66° Bé., in two absorption towers

arranged similarly to Gay-Lussac towers. The alcohol is absorbed in the first column and the ether in the second. The latter is recovered by distillation *in vacuo*. According to patent of addition 5717, the acid containing the ether is diluted with water in the proportion of 1 to 2 molecules of water per molecule of acid before distillation. In British patent 13,605/1905, of Soc. Jean & Co. and G. Raverat, the absorption of the vapours in columns by means of glacial acetic acid or phosphoric acid is proposed. The solvents are partially recovered from the absorbent acids by dilution with water to 30° to 40° Bé., whilst those soluble in water are recovered by distillation. A special apparatus for carrying out this and similar processes is described by Bouchaud-Praceiq in Austrian patent 29,829 and Swiss patent 33,684. In French patent 301,262, the Soc. de Tubize proposes the use for absorption of strong sulphuric acid of 62° Bé., the later concentration of which offers no difficulties. According to British patent 15,372/1905 and French patent 356,835, J. Douge proposes to remove the solvents from the threads wound on bobbins by diffusion on the counter-current principle. In air containing alcohol and ether vapour these are stated to be recovered in a special suction apparatus by centrifugal force, or by impact on baffles inserted in the gas current. According to French patent 349,843, Aurenque collects the alcohol and ether vapours in special conduits in the lower portion of the building and condenses them by cooling to – 10° C. According to British patent 14,087/1906, German patent 194,825, Austrian patent 32,783, U.S. patent 828,155, and French patent 361,568, Vittenet passes the thread during spinning through two concentric tubes, relatively rotatory, which are each provided with a slit along their entire length and which carry radial openings at the top which are closed when the slits are closed. The outer tube rests on a conical portion of the spinning tube, from which it can be lifted, and is carried by angle irons adjustable on rollers. The arrangement will be quite clear from Fig. 80. In German patent 196,699, and French patent 386,833, Bucquet proposes to absorb the solvents by means of liquid fat or fatty acids. In British patent

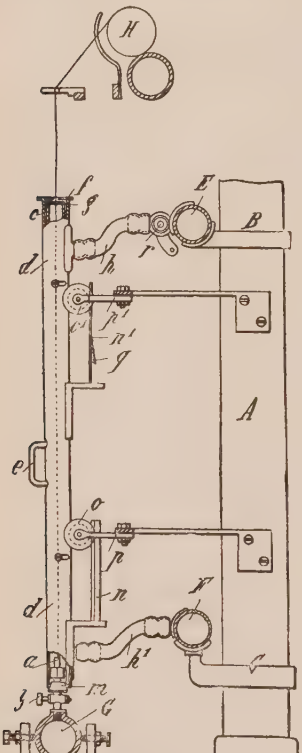


Fig. 80. Vittenet's Solvent Recovery Machine

5020/1907, German patent 203,916, Swiss patent 39,587, Austrian patent 38,532, and French patent 372,889, Diamanti and Lambert describe a spinning machine in which special attention is paid to the recovery of the solvents. It is shown in section in Fig. 81, and is characterized by a channel formed by fixed screens *g* and louvre-like movable screens *h* immediately above the nozzles *c*, with a tube *j* placed at the bottom of the channel for removing ether vapour, and a

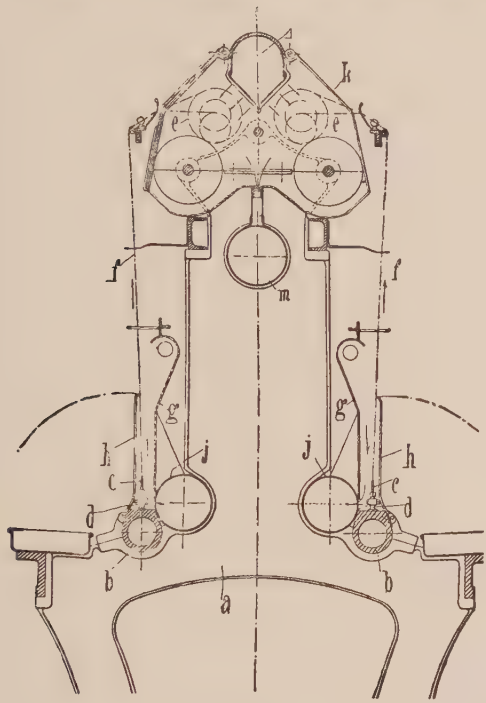


FIG. 81. DIAMANTI AND LAMBERT'S SOLVENT RECOVERY MACHINE

helmet-shaped casing *k* with narrow inlets for the threads *f*, and a tube *l* at the top of the casing for discharging alcohol vapour. Similar arrangements for encasing the spinning machinery are described in British patent 11,729/1909, Austrian patent 47,780, and French patent 412,887, of the Société de Tubize, and in French patent 416,064 of Fournaud. The various plants of the Soc. l'Air Liquide utilize cold and compression (British patent 5395/1909, U.S. patent 1,040,886, French patent 397,791, and patent of addition 11,267 ; also French patent 413,571, German patent 229,001, and French patent 435,079). This is a less satisfactory method of solving the problem. Compression-refrigerating machines are also employed according to French patent

387,054 of the Chardonnet Co. In French patent 401,182, Crépelle-Fontaine describes an absorption tower for the solvent vapours containing superposed divisions, and in French patent 396,664, Swiss patent 45,485, and U.S. patent 951,067, he describes a special distilling column for the recovery of the solvents from their admixture with the sulphuric acid which is used as an absorbing agent. According to French patent 376,785, A. de Chardonnet uses three towers or chambers for absorption, the last of which contains water containing alcohol, which is said to be a particularly good absorbent for ether. After enrichment with ether, the mixture is passed through the second chamber and finally through the first chamber in counter-current to the air discharged from the spinning machines, with which it comes into intimate contact. Reagents for fixing alcohol, such as calcium chloride, may be added. According to German patent 207,554 and French patent 377,673, the same inventor uses high-boiling alcohols, such as amyl, butyl and propyl alcohol, as absorption agents. According to his French patent 413,359, these solvents are also used; according to this patent the alcohol and ether vapours contained in air are recovered by means of an arrangement according to which the nozzles are not placed in long rows but in circles on rotary plates, similarly to the arrangement in the patent described on page 138, of Soie Artificielle d'Obourg and M. Denis. According to German patent 203,649, and French patent 367,803, the Chardonnet Co. recovers the alcohol and ether still present in the wound thread by rinsing this with pure water or with water containing a salt of potassium, magnesium or other metal in solution. A special contrivance for carrying out this process is described in patent of addition 7469. In French patent 371,985, the same Company has claimed protection for a recovery process in which the products are treated with a current of steam, which may be superheated, at ordinary or reduced pressure, and the expelled volatile solvents are condensed in coolers or columns. In French patent 420,086, Sauverzac proposes to absorb the vapours of solvents by means of an aqueous-alcoholic solution of a chloride such as aluminium or sodium chloride or of an organic chloride such as carbon tetrachloride. It is not, however, stated whether these solutions are to serve as a precipitation bath or for absorption at a later stage. A similar process is described by Delpech in Belgian patent 263,359, and also by Chandelon, in German patent 254,913, and Belgian patent 254,511, who uses chlorine-, bromine-, or nitro-derivatives of aliphatic or aromatic hydrocarbons, boiling above 100° C. We may also mention here the proposal by Bergé in Belgian patent 250,816 to use formic acid, acetic acid, and amyl-alcohol, tetrachlorethane and nitrobenzene as absorption agents. According to British patent 23,995/1911, German patent 241,973, and French patent 435,742, A. Wohl passes the gases over fresh quantities of cellulose ester. Duclaux, who uses methyl or ethyl formate as solvents in his spinning process, which has already been described, mentions various processes for the recovery of these solvents by means of alkalis in French patent 439,721, and patent of addition 16,214, and also in German patent 256,857, and U.S. patent 1,127,871.

In Belgian patent 253,831, Lointier proposes the use of lactic acid

or its derivatives as absorbing agents. In Belgian patent 253,805, the same inventor describes a contrivance by means of which the vapours of the solvents are expelled in highly-concentrated admixture with air. According to British patent 7098/1915, H. Frischer passes air, laden with vapours of the solvents, through liquids having the same or approximately the same composition as the solvents to be condensed. A special contrivance for determining the specific gravity of air, loaded with vapours, contained in the pipe system discharging from workrooms or spinning machines, is described by Barbet et Fils in British patent 101,875. According to Persch (Swiss patent 78,099) it is possible to separate alcohol and ether almost completely from one another by first warming the mixture to the boiling point of the solvent in question and then immediately cooling strongly. According to British patent 129,024, Craig, Robertson, Masson and Drummond recover ether from air by saturating it with alcohol vapour and then absorbing in absorption towers and so forth, with alcohol cooled below 0° C. A special arrangement of chamber-towers for absorbing vapours of solvents by means of sulphuric acid is described by A. Lehner in German patent 303,396. The chambers are connected in series, and the enriched sulphuric acid from the lowest chamber is periodically removed by a syphon or other discharging contrivance, whereupon the chamber is filled with acid from the upper chamber which is emptied in the same manner. In British patent 127,309, and U.S. patent 1,315,700, Brégeat describes an absorption agent consisting mainly of phenols. An arrangement for the continuous operation of the process is described by him in U.S. patent 1,315,701.

Activated carbon is much used for the purpose to-day, and has proved very satisfactory.

In general, it may be stated with regard to solvent recovery that the processes using liquid absorbents usually give better results than processes working by refrigeration or compression. The best method appears to be the use of active charcoal, by means of which 80 to 85 per cent of the solvents are usually recovered. When producing the spinning solution it is important to use a solvent mixture of the most favourable composition, that is, one containing as little as possible of the more readily volatile solvent. The best recovery processes usually only permit of the recovery of 70 to 80 per cent, at most.

Other By-products. The purification or recovery of other by-products of collodium silk manufacture has been the subject of various patents. We may mention Claessen's German patent 300,595 for the purification of the waste spirit; French patent 354,398, and Austrian patent 25,239 of the Chardonnet Co., for the recovery of the cotton wool and gauze used in the

filter presses ; French patent 410,652 of the same company for the recovery of nitrogen and sulphur compounds from the denitration baths, and finally German patent 234,672 of the Soc. Soie de Tubize for the purification of the aqueous effluents obtained in the manufacture of collodium silk.

CHAPTER X

MANUFACTURE OF CUPRAMMONIUM SILK

As indicated by its name, the basis of this process is the solubility of cellulose in ammoniacal copper oxide, which was discovered by Schweizer in 1857. (*Journ. f. prakt. Chem.*, 1857, pages 109 and 344.) We will first briefly consider the formation and behaviour of copper compounds concerned in the process.

Interaction of Copper Salts and Alkali Hydroxide Solutions. With a slight excess of dilute solutions of potassium or sodium hydroxide, solutions of cupric salts form a voluminous, light-blue precipitate of copper hydroxide, $CuO \cdot H_2O$ or $Cu(OH)_2$, which is insoluble in excess of the reagent. In the case of very concentrated solutions of the hydroxides only, the precipitated copper hydroxide dissolves to a dark-blue solution, particularly on warming. The precipitate is also soluble in excess of alkali hydroxide in presence of glycerine. Pure copper hydroxide does not dissolve in ammonia alone, but solution is easily effected in presence of a little ammonium salt. (See later under the heading of " Ammoniacal Copper oxides.") Copper hydroxide is a complex base, which is partially or completely dissolved by various metallic salt solutions, with formation of basic salts which are usually amorphous, differing in this way from those produced from $4CuO \cdot H_2O$. Under certain conditions of concentration calcium hydroxide also precipitates green $Cu(OH)_2$ from copper sulphate solution. Copper hydroxide is also precipitated by freshly precipitated and well-washed calcium carbonate. A compound of the formula $CuO \cdot 2H_2O$ is also known, and is produced if copper sulphate solution is precipitated by potassium hydroxide solution and the precipitate washed until the caustic alkali is completely removed. The precipitate always contains traces of sulphuric acid.

Copper Salts and Ammonia. When an excess of the reagent is avoided, ammonia precipitates from cupric salt solutions a light green, more or less powdery precipitate, which readily settles in contrast to the voluminous precipitates of hydroxide

formed with alkali hydroxide; this precipitate consists of basic copper sulphate, $CuSO_4 . Cu(OH)_2$. The precipitate readily dissolves in excess of ammonia to a deep blue liquid which contains the compound $CuSO_4 . 4NH_3$ with 1 or $1\frac{1}{2}$ molecules of H_2O. This compound is separated from the solution in the form of dark violet-blue crystals by adding an excess of alcohol. If the concentrated solution of $CuSO_4 . 4NH_3$ is diluted with a little water, a dark bluish-violet precipitate is gradually formed, consisting of basic cuprammonium sulphate, $4CuO . SO_3 . 2NH_3 . 5H_2O$. If to a concentrated copper sulphate solution ammonia is added, until the precipitate which is first formed is almost completely dissolved, and the liquid allowed to stand for some time, a bluish-violet precipitate is formed, which probably represents the compound $CuSO_4 . 4NH_3$ contaminated with a little $CuSO_4$ and $(NH_4)_2SO_4$. According to Perman, so-called complex salts are present in the ammoniacal solution, which easily decompose on heating. The cation $Cu'' + NH_3$ is less complex than $Cu' + NH_3$. Dowson and Crae assume that the complex salt $Cu4NH_3 . SO_4$ and the base $Cu2(NH_3)(OH)_2$ are present in the solution and dissociate to form $Cu4NH_3 + SO_4$ and $Cu2NH_3 + 2(OH)$. The compound $CuSO_4 . 4NH_3(+ aq)$ is most easily obtained by passing a very strong current of ammonia gas into a well-cooled concentrated copper sulphate solution until the whole of the copper is finally precipitated, and then washing the precipitate with aqueous ammonia and drying it over quicklime. The compound crystallizes in transparent dark-blue prisms which readily dissolve in a little water, but form a precipitate of basic sulphate when highly diluted.

It is not possible to combine more than 5 molecules of NH_3 with $CuSO_4$. The number of combined NH_3 molecules decreases with increasing dilution and decreasing concentration of the ammonia proportionately to the $CuSO_4$.

The solution of copper sulphate in excess of ammonia naturally also contains ammonium sulphate. It does not dissolve cellulose alone, but does so in presence of sodium or potassium hydroxide. (Baubigny, *Compt. rend.*, 1887, page 1616; Bouzat, *Ann. Chim. Phys.*, 1903, page 372.) A solution of pure

basic cupric sulphate in aqueous ammonia, on the contrary, dissolves cellulose.

Ammoniacal Copper Oxides. These compounds are obtained by treating copper, copper oxide or copper hydroxide with aqueous ammonia. Solution does not usually, however, take place without the addition of certain auxiliary substances. Copper, in the form of copper filings or of cementation copper, dissolves in aqueous ammonia if air is passed through the solution. Solution occurs particularly easily in the presence of a little ammonium salt, such as NH_4Cl. It is assumed that copper is first oxidized to Cu_2O and then to CuO and that the ammonia is oxidized to HNO_2, so that both cupric nitrite-ammonia and cupric nitrate-ammonia are finally formed. The solution contains a colloid. According to the statements of A. Lecoeur in British patent 16,442/1906, French patent 374,277, and U.S. patent 863,802, it is advantageous to add initially as much sodium hydroxide as corresponds to the nitrous acid formed during the process. It is stated that the sodium nitrite which is formed reacts with ammonia and copper in the cold to form nitrogen, copper oxide, sodium hydroxide and water, so that sodium hydroxide is always re-formed and consequently only requires to be added in extremely small quantities. Copper oxide, CuO, and copper hydroxide, $Cu(OH)_2$, behave quite similarly. The solution of these in aqueous ammonia also occurs more readily in presence of ammonium salts, and preferably with simultaneous passage of air through the liquid. The addition of a small quantity of acid suffices, as this, of course, immediately forms an ammonium salt. Carbonic acid is also very effective. The addition of a little platinum chloride or of iron acts in the same manner as ammonium salts. The solubility depends on the concentration of ammonia, and Bonsdorff (*Zts. f. anorg. Chem.*, 1904, page 182), gives the following figures for 25° C.—

Gm. equivalents of NH_3 per litre	2·540	1·965	1·280	0·973	0·870	0·540	0·391
Gm. Cu per litre	6·26	6·28	4·13	3·36	3·08	2·36	2·04
Gm. equivalents of $Cu(OH)_2$ per litre	0·197	0·166	0·129	0·106	0·097	0·074	0·064

Some cupric nitrate-ammonia is always formed as a by-product. Apparently, ordinary copper oxide is rather more easily dissolved than the precipitated oxide, but moist $Cu(OH)_2$ is more easily dissolved than when dry. Ignited CuO is less easily dissolved. On the other hand, CuO is said to be more easily soluble in ammonia in presence of nitrogen.

For the technical production of ammoniacal copper oxide solutions, see page 233 *et seq.*

When it contains much copper the dark azure-blue cuprammonium solution (Schweizer's reagent) contains the compound $Cu(OH)_2 . 2NH_3$ if a large excess of ammonia is present and the compound $Cu(OH)_2 . NH_3$ if less is present. When much ammonia is present the compound $CuO . 4NH_3 + 4H_2O$ is also probably present and may be obtained in the crystalline condition, in the form of long dark-blue needles which easily deliquesce in the air and are decomposed by pure water. In the air they are gradually decomposed with formation of nitrite and cupric carbonate-ammonia. At the ordinary temperature the solution does not change if it contains colloid only, but on long standing of a concentrated solution (which is 0·08 normal, and contains 7 molecules of NH_3 per molecule of CuO), a precipitate of $Cu(OH)_2$ separates. Copper hydroxide is also precipitated by diluting considerably with water, and also on adding alkali hydroxide solution, the necessary quantity of which is the greater the more ammonia is present in solution. Sulphur dioxide precipitates almost the whole of the copper from solution in the form of Cu_2O. Copper is precipitated by metallic zinc and cobalt, whereas the reduction caused by tin, arsenic and cadmium is only slight and no reduction occurs with lead. Iron reduces the solution incompletely and does not act at all on the pure solution, though it precipitates copper in presence of NH_4Cl, NaCl, KNO_3 or K_2SO_4 if no large excess of ammonia is present.

In German patent 230,941, Austrian patent 57,698, and U.S. patent 986,017, the Vereinigten Kunstseidefabriken, A.-G. Kelsterbach, propose the use of ammoniacal cuprous chloride, alone or together with ammoniacal copper oxide, for dissolving cellulose.

Cuprammonium-cellulose Solutions. It has already been mentioned that a solution of copper sulphate in excess of ammonia does not dissolve cellulose alone, but does so in the presence of alkali hydroxide ; and also that a solution of basic cupric sulphate in excess of ammonia dissolves cellulose. If one observes the process of solution under the microscope one first sees that the cotton fibres, which are usually twisted, untwist, and at the same time become considerably shorter. The cuticle forms numerous transverse folds and bursts at many places, after which the burst parts contract to form folded rings. At the same time, the inner cell wall forms obvious transverse folds, after which barrel-shaped swellings occur between the cuticular rings. (See Fig. 82.) This is followed by a more or less rapid complete solution of the cell wall and the inner pellicle, leaving, in the case of unbleached cotton, an undissolved residue, consisting of the remains of the cuticle and of the insoluble albumens. In bleached cotton the latter are no longer present in appreciable quantity, as they have been destroyed (see page 29). The various kinds of cotton show no appreciable differences, apart from possible variations in the speed with which they are dissolved. A few fibres only, in every kind of cotton, occasionally show abnormal behaviour.

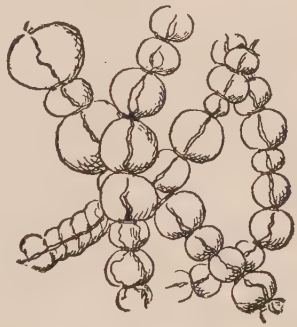


Fig. 82. Cotton Fibre Gelatinized by Cuprammonium Solution
Magnification 50

It is still not quite certain what kind of cellulose compound is present in this cellulose solution. Lehner (*Zts. f. angew. Chem.*, 1906, page 1584), was of opinion that cellulose combined with copper oxide or hydroxide to form a copper alcoholate similar to sodium alcoholate, which dissolved in ammonia to form a water-soluble cuprammin base. Similarly, Traube assumes (*Ber. d. Chem. Ges.*, 1921, page 3220 ; and 1922, page 1899), that cellulose unites with copper hydroxide and ammonia to form copper tetrammin hydroxide, which unites in turn with cellulose to form copper tetrammin alcoholate. Others assume

the formation of a so-called inner complex salt, in which the copper, on the one hand, unites immediately with the cellulose to form an anionic cellulose-copper complex, which unites with the cation $Cu(NH_3)_4$ to form a true salt, a cellulose-copper complex salt $(C_6H_7O_5Cu)_2Cu(NH_3)_4$. (See H. Ley, *Zts. f. Elektrochem.*, 1904, p. 954 ; Hess and Messmer, *Ber. d. Chem. Ges.*, 1921, p. 834 ; 1922, p. 2432 ; 1923, p. 587). The French chemist, Levalois, had already observed the high optical rotary power of these cellulose-copper oxide-ammonia solutions in 1884. The optical rotation is dependent on the temperature, the contents of cellulose and the amount of dissolved copper. In the presence of 4 molecules of $C_6H_{10}O_5$ and 10 molecules of $Cu(OH)_2$ per 100 litres of solution, Hess found the optical rotation of the purest cotton cellulose to be $[\alpha]_D = -3{\cdot}36^\circ \pm 0{\cdot}01$ (*Zts. f. angew. Chem.*, 1924, page 993 ; *Cellulose-Chemie*, 1925, page 42). The circumstance that the optical activity occurs immediately after solution and remains permanently constant suggests that no chemical change of the cellulose molecule occurs during the solution process. In agreement with this supposition, the cellulose which is reprecipitated from the solution may be considered to be chemically unchanged ; more particularly the X-ray spectragraphic diagrams of the regenerated cellulose are said to correspond almost completely with those of the original material. However, R. O. Herzog (*Ber. d. Chem. Ges.*, 1924, page 330 ; *Naturwissenschaften*, 1924, page 957), concludes from the slight alterations of the cellulose space lattice by solution in Schweizer's reagent that chemical change of the molecule has occurred. It is, however, possible that such slight changes, as also the strong attraction for dyestuffs, the greater hygroscopicity and the fact that the regenerated cellulose is more readily hydrolized, may be due to physical or colloid-chemical causes, such as swelling phenomena. Similar remarks apply to mercerized cellulose.

It may be mentioned that apart from cotton, wood-pulp, in the form of crinkled or tissue paper, has been successfully used for the manufacture of cuprammonium silk, more particularly by the stretch-spinning process (see page 251 *et seq.*). Good pure sulphite pulp, such as is manufactured, for example,

by the Zellstoffabrik Waldhof, especially for artificial silk manufacture, dissolves readily in ammoniacal copper oxide and produces an excellent, high quality, artificial silk thread on spinning the solution.

The process mentioned by Müller and Wolf of producing cellulose from hop-bine fibre, according to British patent 5659/1912 and German patent 256,351, was already mentioned on page 57. They state that the fibre is easily isolated by boiling the hop-bines with soda and soft soap.

Although, as will be gathered from the above information, much remains to be explained from a scientific standpoint regarding the composition and the reactions of the various compounds, the fact that a specific solvent for cellulose had been found formed the basis for a new process of artificial silk manufacture which was destined to play an important part, more particularly in the German artificial silk industry.

In French patent 203,741 of Louis Henri Despaissis, the use of cuprammonium cellulose solutions in general for the production of fibres, in place of Chardonnet's collodium solutions, is claimed broadly. Although the inventor mentions the necessary steps to be taken with regard to the raw material and its pre-treatment, the filtration of the spinning solution, spinning, spinning baths, winding, washing, de-coppering, recovery of the copper, drying and after-treatment of the fibres, and so forth, his statements on the details of the various processes are in very general terms. The process of Fremery and Urban, as described in Pauly's German patent 98,642/1897, and the corresponding foreign patents, (British patent 28,631/1897, French patent 272,718, U.S. patent 617,009), and completed by further patents of Fremery, Urban and Bronnert, devotes much attention to the production of a satisfactory spinning solution. The discovery of more particular importance was that at low temperatures cellulose dissolves more readily and in larger quantity in ammoniacal copper oxide solutions than at higher temperatures.

When sketching the development of the process in the Historical Section, page 10, we already indicated that it had undergone various fundamental alterations in the course of its

development. Three main stages of development can be distinguished, namely, the old process of Despaissis and of Fremery and Urban, the improved process on the same general principles of the Elberfelder Glanzstoffabriken and other firms or inventors, and finally the modern stretch-spinning process in its present form.

In the following descriptions, however, as in the case of those of other forms of artificial silk, it has been found convenient to divide the information according to the various stages of manufacture.

Pre-treatment of Cellulose. In the case of cotton the mechanical and chemical purification described in an earlier chapter (page 61 *et seq.*) is mainly followed. The solubility of the cotton was later considerably increased by special pre-treatment, which also considerably reduced the time required for solution. Whilst originally as much as 8 days were required for this purpose, the solution of suitably pre-treated cotton can now be carried out with stirring and thorough cooling below 4° C. in 8 to 10 hours. Cotton waste from spinneries, and so forth, could also be used for the purpose after suitable pre-treatment.

A special form of pre-treatment was first described by Fremery and Urban. According to their British patent 6557/1899, German patent 111,313, Austrian patent 3636, French patent 286,925, and U.S. patent 657,818, the solubility of cellulose could be increased by energetic treatment with oxidizing or reducing bleaching agents, such as sulphites, hypochlorites, chlorine water and so forth. The above-mentioned patentees, jointly with E. Bronnert, patented a process in British patent 13,300/1899, German patent 119,098, Austrian patent 8596, French patent 292,988, and U.S. patent 646,351, according to which the cellulosic material was thoroughly mercerized with concentrated alkali at a low temperature, then bleached, washed and dissolved without previous drying. According to the additional patent (British patent 18,884/1899, German patent 119,099 and Austrian patent 8596) the process is modified by first slightly bleaching, with avoidance of oxidation, the cellulosic material which has been de-greased with weak alkali solution, then thoroughly mercerizing it with concentrated cold alkali solution, then washing and finally dissolving without drying. A similar process is described by R. Langhans in German patent 140,347 and U.S. patent 672,946. In French patent 345,687, J. Foltzer claims the following pre-treatment of cellulosic material: To 100 kg. of cotton, which are placed between perforated metal sheets in a closed container, there is added a solution of 30 kg. of soda and 50 kg. of

caustic soda in 1000 litres of water at 119° C., which is maintained in circulation through the cotton at a pressure of about ½ atmosphere. The action is said to require about 4 hours, but may be shortened if the material under treatment contains at least 12 to 15 per cent of moisture. Cotton which has been pre-treated in this manner is said to dissolve in less than 24 hours in the cold in ammoniacal copper oxide, or in zinc chloride solution, to form an 8 to 10 per cent solution. In British patent 22,422/1906, German patent 187,263, U.S. patent 908,751, French patent 361,048, and additional patent 6629, E. Crumière describes a process which reminds one of the above-mentioned patent of Fremery and Urban, according to which the fibrous material is treated with ozone in presence of alkalis before solution. The process can, for example, be carried out simply by dipping the cotton to be treated into a bath of soda solution through which a stream of ozone or ozonized air is passed. According to the pre-treatment process described in U.S. patent 879,416, by G. L. Schäfer and A. Schäfer, the cellulose is heated with alkalis and benzine under pressure, washed, treated with weak hydrogen peroxide solution, washed again, then bleached with dilute hydrogen peroxide solution, again washed, centrifuged and entered into the cuprammonium solution whilst moist. In his British patent 17,164/1905, French patent 357,171, U.S. patent 813,878, and in his British patent 6072/1906, and French patent 364,066, E. W. Friedrich proposes as pre-treatment for the cellulose almost everything which could be imagined ; namely, conversion into oxy-, hydro-, hydrate, colloidal, or mercerized cellulose.

The cellulose, after pre-treatment by one or the other method, was formerly always dissolved in a separately prepared and finished cuprammonium solution.

Preparation of the Cuprammonium Solution. The process was carried out, for example, as follows: Aqueous ammonia solution was poured over copper turnings in tall iron cylinders, provided with a cooling jacket, and of 500 to 1000 litres capacity. Similar apparatus was described, for example, by E. Mertz in Swiss patent 34,700 and French patent 364,911 ; and by the Société an. La Soie Nouvelle in British patent 20,408/1906, French patent 369,973, and U.S. patent 850,695. The quantities of copper which are recommended vary from " at least about 15 gm." to a maximum of 40 to 50 gm. of copper per litre of liquid containing 15 to 30 per cent of ammonia. The average quantities which were ordinarily used were probably 30 to 35 gm. of copper per litre of solution containing about 25 per cent of ammonia. The temperature of the mixture was maintained at 0° C., or rather lower, by

refrigerated brine which circulated in the jackets of the apparatus, and air at 1 to 1·5 atm. pressure was blown into the liquid from below. The heat which was thus evolved was removed by constant further cooling. The temperature of the batch was not supposed to exceed + 5° C. (See British patent 1763/1900, German patent 115,989, Austrian patent 10,263, and U.S. patent 658,632, of Bronnert, Fremery and Urban.) The treatment lasted for at least 12 hours, but the injection of air was frequently interrupted during the treatment for 1 to 1½ hours. The air expelled at the upper end of the cylinder naturally contained considerable quantities of ammonia and was passed through water or dilute sulphuric acid in order that this might be recovered as aqueous ammonia or ammonium sulphate. (For further particulars, see "Recovery of Chemicals," page 256.)

Before the cellulosic material was introduced into the cuprammonium solution, this was at a later date reinforced by the addition of copper sulphate and sodium hydroxide, as it had in the interval been found that a considerable saving of copper could thus be effected and the solution of the cellulose could be accelerated. To each 100 litres of cuprammonium solution, for example, 50 litres of a 20 to 25 per cent copper sulphate solution and 7 to 8 litres of a 35 per cent sodium hydroxide solution were added. The pre-treated cotton was introduced into this solution to the amount of about 10 kg. of air-dried cotton per 100 litres of solution.

It is obvious that improvements on this process were relatively easy and necessary. It was very important economically to reduce the consumption of copper and of ammonia considerably, which could be effected either by suitable composition of the solutions or by more complete recovery of these chemicals. Such attempts led to a number of considerable changes in the original process. A large number of patents dating from the first years of the present century were inspired by the endeavour to obtain solutions containing as much copper as possible with a low percentage of ammonia, which should be capable of dissolving a maximum quantity of cellulose. Experience showed that in general cuprammonium

solutions dissolved the more cellulose the greater their concentration in copper, and that on the other hand a large excess of ammonia was prejudicial.

According to French patent 344,138, M. Prud'homme had already found that ammoniacal copper solution dissolved cellulose much more rapidly and in considerably greater quantity if it also contained caustic soda or caustic potash. He states that not more than 2 molecules of caustic potash should be used per molecule of copper, and that the quantity of dissolved cellulose was the greater the more closely the quantity of alkali approximated to this proportion. The addition of alkali is also recommended in the patents of A. Lecoeur already mentioned on page 227. In British patent 14,143/1908, French patent 401,741 and U.S. patent 947,715, the Soc. an. " Le Crinoid " describes the manufacture of two standard solutions. The first is obtained by adding ammonia and caustic alkali to a solution of a copper salt, and then dialysing, by which means a colloidal solution of ammoniacal copper oxide is obtained containing 12 gm. of copper per litre, and capable of dissolving 30 gm. of cellulose per litre. A second solution was to be obtained, according to the process of Lecoeur already referred to (French patent 374,277), by the action of ammonia and atmospheric oxygen on copper in presence of a little caustic alkali ; this solution was said to dissolve 110 to 120 gm. of cellulose per litre. The two solutions were then to be mixed in such proportions as were required for the quality of thread which was to be produced.

In British patent 2080/1900, German patent 119,230, Austrian patent 6064 and U.S. patent 672,350, Bronnert, Fremery and Urban recommend the use of ammoniacal copper carbonate solution in place of copper oxide solution for dissolving cellulose, it being already known that solutions of other copper salts in ammonia were capable of dissolving cellulose. (See, for example, *Vierteljahresschrift der Naturforschenden Gesellschaft in Zürich*, 1857, page 396 ; and E. Schweizer, *loc. cit.*, 4th year, page 1859.) According to P. Spence & Sons, Ltd. (British patent 25,532/1911, German patent 264,952, French patent 449,801 and Belgian patent 250,441), a cuprammonium solution particularly suitable for the solution of cellulose can be obtained by the use of copper in an extraordinarily fine state of division, as obtained from copper sulphate or the like by means of reducing salts such as titanium sesquisulphate, chromous sulphate, and so forth. The finely divided copper so precipitated is washed and then treated with ammonia and air in presence of water. According to British patent 25,533/1911, German patent 264,951, French patent 449,803, and Belgian patent 250,442, of the same firm, the process may be carried out by precipitating the copper in an extremely fine state of division in and on the mass of the cellulose.

The separate preparation of the solvent liquid, that is, of the cuprammonium solution, and of the cellulose solution was retained for a long time, but it was soon found advantageous to

replace the metallic copper by precipitated copper hydroxide which had been purified from admixed salts by washing with water. It was, however, found necessary to carry out this process in two stages, as on the one hand, the hydroxide directly precipitated by caustic alkali forms a voluminous gelatinous precipitate which does not settle well, and cannot consequently be well washed, even by decantation ; and on the other hand, ammonia does not precipitate a pure hydroxide but a light-green basic sulphate, $CuSO_4 . Cu(OH)_2$, which, with excess of ammonia, does not form cuprammonium but a copper ammonium sulphate such as $CuSO_4 . 4NH_3 . H_2O$ which is not suitable for dissolving cellulose. The process adopted was, therefore, first to precipitate a basic salt with ammonia, which offered the advantage that it settled readily, to wash this free from the ammonium sulphate produced during the reaction and then to convert it into copper hydroxide by cold caustic soda, during which process alkali sulphate was again formed and had once more to be removed by washing. In this way it was found that less copper and less ammonia sufficed for dissolving a given quantity of cellulose. Moreover, the advantage was gained that it was not necessary to cool.

Certain firms preferred, however, to obtain a solution of copper hydroxide and ammonia in one operation by stirring together ammonia, caustic alkali solution and copper sulphate, and removing the sodium sulphate which was formed by strong cooling and consequent crystallization.

For example, in each 1000 kg. of an aqueous solution containing about 20 per cent of ammonia and 6 to 7 per cent of caustic soda, 140 kg. of finely ground copper sulphate were dissolved with stirring and strong brine cooling, which caused the sodium sulphate which was formed to separate as a crystalline magma. The cotton was dissolved in the clear solution, decanted from the crystalline mass, in a closed vessel provided with a stirrer ; this operation also took place with careful cooling. This method of working offered the advantage that the double washing for the removal of sulphates was avoided, but on the other hand intensive cooling was required, apart from the other disadvantage that the crystalline mass of

separated Glauber salt contained appreciable quantities of copper which could only be removed and recovered with difficulty.

The proposal made by E. W. Friedrich in the patents already referred to on page 233, and by W. Traube in British patent 356/1912, German patent 245,575, and patent of addition 252,661, Austrian patent 56,625, Swiss patent 58,882, French patent 438,632, U.S. patent 1,064,260, and Belgian patent 241,976, to replace the ammonia used for solution by amines, can only be carried out, if at all, with aromatic amines, such as aniline, on account of the high production cost of aliphatic amines ; aromatic amines, can, however, only replace the ammonia to a relatively small extent, for which reason the process has remained technically unimportant.

In British patent 8910/1906, German patent 185,294, Austrian patent 30,496, French patent 362,986, and U.S. patent 863,801, A. Lecoeur proposes to submit the cuprammonium solution to dialysis before introducing the cellulose. It is alleged that in consequence of the removal in this manner of all crystalloids which interfere with the stability of the solution, stable solutions are obtained which can be stored without cooling. Purification of the solution by dialysis is also recommended in the patents already referred to of the Soc. An. " Le Crinoid " (see page 235).

According to the statements of the Glanzfäden A.-G., Berlin, a stable copper salt, particularly suitable for the manufacture of cellulose solutions, can be obtained without artificial cooling if the copper sulphate solution is treated with a quantity of sodium hydroxide solution insufficient for the complete precipitation of the copper, and if dissolved bicarbonate or other acid salt is then added, after which the precipitation of the copper salt by further addition of caustic soda solution can be completed. It is stated that if the precipitated product is dissolved in ammonia, preferably after previous admixture with the cellulose, solutions containing 15 per cent of cellulose are easily obtained. In this solution process, also, no cooling is required. (See British patent 29,385/1909, German patent 269,787, Austrian patent 58,299, Swiss patent 51,246, French patent 410,882, and U.S. patent 1,000,827.)

Another process which is carried out without special cooling is that described by J. Foltzer in German patent 229,677, according to which copper is sprayed with ammoniacal liquor, with exposure of a large surface, in an atmosphere saturated with ammonia gas. The apparatus used for the purpose is shown in Fig. 83. The ammonia liquor in the container *a* is aspirated by the injector *A*, and injected in the form of a spray *B* over the copper shavings *b* placed on a sieve *E* in the closed container *D*. Copper is thus dissolved as a cuprammonium solution which flows back to the container *a*. The ammonia vapours which escape from the container *D* are carried by the pipe 2 to the container *F*, in which they are absorbed by water. Any slight traces which remain unabsorbed may either be discharged to the outer air through the cock 3, or may be passed through sulphuric acid, or still more suitably may be aspirated through the cock 4 and returned with the ingoing air to the container *a* by means of the injector *A*. This treatment is continued

until the cuprammonium solution in *a* attains a specific gravity of 1·004 to 1·005 at + 20° C.

Long before Foltzer devised this process, the Soc. Générale pour la Fabrication des Matières Plastiques pointed out the advantages of working in an atmosphere saturated with ammonia, and constructed an apparatus for carrying out their process, also without cooling. By simultaneously treating the copper with air saturated with ammonia and treating cellulose with the liquid which was produced they easily obtained in 24 hours, according to their patent specification, a solution

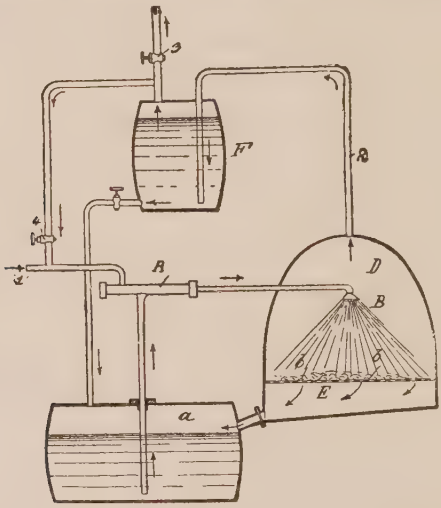


Fig. 83. Foltzer's Apparatus for Preparing Cuprammonium Solution

containing about 65 gm. of cellulose per litre. (See British patent 14,525/1899, German patent 113,208, and Austrian patent 2739.)

Solution of Cellulose in Cuprammonium Solution. The cellulosic material was then mixed intimately with the cuprammonium solution with cooling, in vessels provided with stirrers which were usually of cylindrical form. A good solution usually dissolved from 5 to 10 per cent of cellulose.

The necessary weighing of the cellulosic material was frequently carried out before bleaching, because it was not re-dried after bleaching, and therefore the dry weight could no longer be simply and accurately determined at that stage. However, weighing before bleaching is also not quite satisfactory, as the loss on bleaching may vary considerably. In

German patent 409,767, R. Schröder therefore proposes to dehydrate the bleached cellulose mechanically to an exactly determinable degree, and to weigh it in this condition. For such dehydration he recommends hydraulic presses such as are used for similar purposes in the dyeing industry, after which the cellulose contents of the pressed cake may be determined more exactly. Screw presses or centrifuges may also be used for the dehydration, but yield less exact results.

If the process given on page 236 is followed for the production of the cuprammonium solution (in which about 140 kg. of finely ground copper sulphate are dissolved with stirring and strong cooling in 1000 kg. of solution containing 20 per cent of ammonia and 6 to 7 per cent of NaOH), the liquid decanted from the separated sodium sulphate crystals readily dissolves 8 to 9 per cent of cotton. The solution process requires 3 to 4 hours only.

According to British patents 4755/1905 and 4756/1905, German patent 183,153, Austrian patent 46,701, French patent 346,722, and U.S. patent 795,526, Société Linkmeyer, Brussels, endeavoured to achieve an easier method of solution by first immersing the cellulose in a less concentrated cuprammonium solution containing caustic soda, in order to gelatinize the fibre and deposit copper on the same, and then dissolving it completely in a more concentrated cuprammonium solution. In French patent 376,065, G. Boucquey describes a process in which cellulose is first caused to swell in a mixture of copper salt, ammonia and caustic alkali. According to British patent 10,545/1907, E. Berenguer alleges that he obtains a more readily soluble cellulose by treating it with water immediately after its production and avoiding drying.

As already mentioned, it was realized that a high percentage of ammonia in the solution was prejudicial. Various attempts were therefore made to obtain solutions containing much copper but as little ammonia as possible.

For this purpose, Société Linkmeyer, Brussels, propose, in German patent 183,557, and patent of addition 187,313, and in U.S. patent 852,126, to remove ammonia from the cellulose solution before spinning, by the action of a vacuum or by blowing in air. After this treatment it is alleged to be possible to spin into a more dilute sulphuric acid of

10 to 20 per cent. According to J. Wetzel's French patent 423,510, it is possible to reduce the previously usual percentage of ammonia of about 6 per cent to 3 per cent. The production of a solution with as little ammonia as possible is also the aim of British patent 27,727/1906, German patent 189,359, French patent 372,002, and U.S. patent 850,571, of E. W. Friedrich. He proposes to work with considerably reduced quantities of ammonia by first preparing a solution of cellulose containing the usual quantity of ammonia and then introducing fresh quantities of cellulose into this solution with the addition of further, relatively small, quantities of ammonia. Follet and Ditzler also claim to obtain solutions containing much copper, but free from excess of ammonia, by the process described in their British patent 22,753/1907, German patent 223,294, Swiss patent 41,238, and French patent 382,859, according to which cellulose is dissolved in an aqueous solution containing caustic soda, together with crystals which are obtained by passing ammonia gas into solutions of copper salts (see pages 225 and 226). According to British patent 24,996/1912, French patent 450,193, and Belgian patent 251,118, B. Borzykowski claims to obtain solutions very rich in copper, and containing but little ammonia, by first producing the hydroxide in the actual solution, in which case he claims that it is readily dissolved (see also J. Foltzer, *Kunststoffe*, 1911, page 303).

The process proposed by R. Pawlikowski in German patent 222,624, Austrian patent 49,170, Swiss patent 49,399, and French patent 403,488, of dissolving cellulose in an ammoniacal solution of copper oxychloride, offered no advantage and has, therefore, not been adopted in practice. The same remarks apply to the process proposed by Vereinigten Kunstseidefabriken A.-G. Kelsterbach and F. Lehner, in German patent 230,941, Austrian patent 57,698, and U.S. patent 986,017, according to which ammoniacal cuprous chloride is used for dissolving cellulose alone or together with cuprammonium solution.

According to E. de Haën (British patent 27,835/1911 and French patent 436,968), potassium hydroxide can be used with advantage instead of sodium hydroxide, as the potassium sulphate which is formed separates completely at the ordinary temperature. According to O. Müller (French patent 451,406, and Belgian patent 251,128) the separation of alkali salts by crystallization can be completely avoided, and a large quantity of ammonia can be saved, by first stirring the copper salt with a common salt solution containing glycerine and then with an aqueous ammonia solution containing caustic alkali.

According to British patents 1265/1908, and 12,253/1908, German patent 216,669, Austrian patent 51,799, Swiss patent 42,305, French patent 386,339, and U.S. patents 977,863, and 978,878, G. Guadagni places moist cellulose above the cuprammonium solution in closed containers and blows air through the solution; this air, loaded with ammonia, passes through the moist cellulose, which is then added to the copper solution after having absorbed a considerable quantity of ammonia. The process is said to offer two advantages; both the cellulose and the solution are alleged to be considerably cooled by the evaporation of ammonia during aeration, and the ammonia contents of the cellulose are said to shorten considerably the period of solution

and to raise the yield. Solution is said to occur still more rapidly if caustic soda solution is also added (British patent 25,986/1910). In British patent 10,164/1907, German patent 231,693, Austrian patent 50,506, French patent 377,326, and U.S. patent 840,611 of Hanauer Kunstseidefabrik G.m.b.H., a similar process is described, according to which the cellulose is soaked in ammonia solution before adding copper hydroxide.

Simultaneous Solution of Copper and Cellulose. An intermediate stage, leading to the process now usually adopted of dissolving the cellulose simultaneously with the copper, is represented by the attempts which were made first to produce copper hydroxide-cellulose, and then to dissolve this in ammonia.

This method was already proposed by E. Bronnert in British patent 13,331/1899, German patent 109,996, Austrian patent 3638, French patent 278,371, and U.S. patent 646,381, according to which a copper hydroxide-cellulose, readily soluble in ammonia, could be obtained by grinding together 1 molecule of copper sulphate, $CuSO_4 . 5H_2O$, or of a similar salt, with 1 molecule of alkali-cellulose, such as is used in the viscose process, or the corresponding hydro-cellulose product. This class of processes also includes that described in German patent 140,347 and U.S. patent 672,946 of R. Langhans, already referred to, and which is characterized thereby that the solvent, consisting of copper oxide-ammonia or nickel oxide-ammonia, acts on the cellulose in presence of free copper hydroxide or nickel hydroxide.

According to German patent 162,866, the J. P. Bemberg A.-G. obtained copper hydroxide-cellulose by mixing the cellulosic material with metallic copper (cementation copper) and converting this latter into the hydroxide on the cellulose. According to this patent, a mixture of cellulose, copper, copper sulphate and alkali-chloride may also be treated with a small quantity of water, and the green basic copper salt so obtained may be converted into the pure hydroxide by alkali ; or the mixture of copper and cellulose may be treated with ammonia, air and a quantity of water insufficient to dissolve the cellulose. According to German patent of addition, 174,508, the process may be considerably improved by replacing metallic copper by cuprous hydroxide. The process

described by W. and V. Mahler in Austrian patent 18,454 is very similar to that described in the above-mentioned patent of Bronnert. According to this process, bleached and mercerized cellulose or alkali-cellulose is intimately mixed with a cold-saturated solution of copper sulphate or other cupric salt, and is freed from the excess of solution after standing for several hours. It is stated that the product then dissolves in ammonia to a concentrated solution.

Finally a further stage was reached when the cellulosic material was intimately mixed with copper hydroxide, obtained by precipitation with ammonia or caustic soda and washing, and both these materials were simultaneously dissolved in aqueous ammonia. Well-washed copper hydroxide was ordinarily used in the form of a moist paste. Alternate layers of cotton and of copper hydroxide paste were introduced into a rotary iron mixing cylinder and the aqueous ammonia solution was added. Per 100 kg. of copper hydroxide, calculated as dry $Cu(OH)_2$, about 130 kg. of cotton and 750 kg. of 25 per cent ammonia were used. The mixing vessels were slowly revolved at a rate of 8 to 10 revolutions per minute, and solution occurred in 4 to 5 hours. The solution was then diluted with about 500 litres of water.

In British patent 28,779/1910, French patent 429,841, Austrian patent 62,164, Swiss patent 57,591 and U.S. patent 1,062,222, the Compagnie Française des Applications de la Cellulose gives the following instructions: A solution of 60 kg. of crystallized copper sulphate in 300 to 400 litres of water is introduced at the ordinary temperature with stirring, and with the addition of some sugar or the like, into 40 litres of caustic soda solution, the strength of which is so chosen that the theoretical quantity of cupric hydroxide is formed. 30 kg. of ground cotton, suspended in about 3000 litres of water, are incorporated with the above mixture in a suitable apparatus, such as a disintegrator, if necessary with the help of compressed air; the copper cellulose so produced, which is said to be capable of storage without change, is separated from the liquid, well ground and dissolved in ammonia, for which purpose about 100 litres of ammonia of 28° Bé. are necessary. Some

caustic soda solution is added at intervals during the process of solution. In this manner it is stated that cellulose solutions of about 15 per cent concentration are obtained.

Cuprammonium cellulose solutions, for example, for the ordinary and for the stretch-spinning processes, are now obtained approximately as follows : An aqueous copper sulphate solution is precipitated with caustic soda solution, whilst cooling with ice, and the whole of the copper hydroxide paste is introduced without washing into a disintegrator, in which it is mixed with moist cotton, which has previously been ground in a disintegrator and dehydrated by pressure until it contains about 40 per cent of water. Per 100 kg. of dry cotton, 260 kg. of copper sulphate, and 230 kg. of 35 per cent caustic soda solution are used. The temperature is carefully maintained at 25° or at most 30° C., whilst the mass in the disintegrator is ground to a very homogeneous paste during about 10 minutes. This paste is then filtered in a filter press, and pressed in a hydraulic press at 180 to 200 atmos. pressure in order to remove the liquor, containing sulphate, from the mass as completely as possible.

Instead of precipitating the copper sulphate solution with caustic soda, sodium carbonate may be used, and the basic copper carbonate so obtained may be treated in exactly the same manner as already described for the hydroxide ; this process has more particularly been used with success for the production of cuprammonium cellulose solutions from wood-pulp. The press-cakes are then disintegrated and dissolved in a vessel with stirrer in 570 to 580 kg. of 25 per cent ammonia, to which 60 kg. of 15 per cent sodium hydroxide solution and 50 litres of 1·5 per cent potassium bi-tartrate solution are added. The sodium hydroxide and the acid potassium tartrate are preferably added after the greater part of the cellulose has dissolved, which occurs after about 5 hours. Solution is complete after a total period of mixing of about 10 hours, and the solution may then be diluted as required. The viscosity and the cellulose contents are first determined and the liquid is then diluted until it contains about 8 to 9 per cent of cellulose. The liquid used for dilution preferably contains 80 per cent of

water, 17 per cent of 35 per cent caustic soda solution, and 3 per cent of 25 per cent ammonia. Stirring is then continued for a time, which may amount to 10 further hours. It is stated that the viscosity is slightly reduced by stirring. The mixture is then repeatedly filtered through fine iron or nickel gauze, and is then introduced into the spinning solution supply tank in which it is freed from excess of ammonia and from gas bubbles by exposure to vacuum. The liberated ammonia vapours are absorbed in dilute sulphuric acid or in water. After subjection to vacuum for 10 to 12 hours the solution may be spun.

An advantage of this method of simultaneously dissolving copper and cellulose, which should not be under-rated, is constituted by the fact that it is necessary to cool but little, if at all, and that the rather expensive use of refrigeration may thus be avoided.

According to German patent 235,219 of the Hanauer Kunstseidefabrik G.m.b.H., basic copper sulphate is used, in a form corresponding to the formula $7CuO \cdot 2SO_3 + 6H_2O$, and one may suitably treat 5 molecules of cellulose and 7 molecules of this basic sulphate with an amount of ammonia which is insufficient to dissolve the copper sulphate alone. According to German patent 260,650, and Austrian patent 64,081, of the same firm and W. Vieweg, the components may suitably be caused to interact in presence of broken ice. In German patent 240,082, T. Eck states that he obtains a more stable cellulose solution by preventing the oxidation of the cellulose, by using for solution a mixture of ammoniacal copper oxide and ammoniacal cuprous oxide solutions. He obtains the latter solution by reducing a portion of the ammoniacal cupric oxide, for example, with hydrosulphite.

It is stated that a particularly complete distribution and intensive mixing of the components may be obtained, more particularly when using copper powder or insoluble copper compounds such as the carbonate or hydroxide, by the use of rapidly rotating mixing machinery, such as colloid mills. By this means it is possible to carry out the production of the cuprammonium solution and the solution of the cellulose in one operation. According to German patent 406,311, Maschinenbauanstalt Humboldt has found that in this case the addition of amino-compounds, such as aniline, has a favourable effect, not only on the production of the ammoniacal copper oxide but also on the solution of the cellulose. According to British patent 9336 1911, and German patent 244,510 of G. Ditzler, it is particularly important to carry out both the solution of the cellulose and all following operations before spinning, in the complete absence of air.

Additions to the Spinning Solution. The important observation was made that by the addition of certain substances to

cuprammonium cellulose solutions these could be made appreciably more stable and more suitable for spinning. It was found that this action was exerted by organic hydroxy-compounds such as glycerine, acetin, chlorhydrin, glucose, tartaric acid, citric acid, oxalic acid, glycollic acid, milk sugar, cane sugar, mannite, dulcite, starch, dextrine and so forth. In practice, glucose was ordinarily used, for example in the form in which it is produced from maize in America, under the name of "capillary syrup," in a comparatively cheap form; and also treacle or similar materials. To a bath of 100 kg. of copper hydroxide and 130 kg. of cotton, about 15 kg. of sugar are added, dissolved in 65 litres of water.

Such additions were first recommended by R. Linkmeyer, P. Friedrich and the Glanzfäden A.-G., Berlin. (See British patents 4104/1909, 14,112/1909 and 145,035; German patents 228,872, and patent of addition 237,716; 241,921, and 306,107; Austrian patents 46,861 and 59,032; Swiss patents 45,764, 48,679 and 79,659; French patents 400,321 and 404,372; U.S. patents 945,559 and 962,770); also the following patents of the British Cellulose Syndicate, Ltd., and Mertz: British patent 1148/1909, German patent 250,596, French patent 411,592, U.S. patent 954,984; the following of Chemische Fabrik Bettenhausen, Marquardt and Schulz; British patent 4872/1909, Austrian patent 41,720, French patent 399,911, and Swiss patent 45,290; of the Hanauer Kunstseidefabrik—German patent 220,711, and U.S. patent 988,430; of H. Bernstein—British patent 15,991/1910, U.S. patent 965,273, German patent 248,303, Austrian patent 60,034, Swiss patent 53,440, French patent 418,282, and U.S. patent 965,557; and finally, the following patents by the Rheinische Kunstseidefabrik A.-G., Aix-la-Chapelle—British patent 18,342/1909, German patents 231,652, 236,537 and 236,816, Austrian patents 54,260 and 54,785, and French patent 405,571. In British patent 6408/1912, German patent 251,244 and French patent 441,963, E. de Haën proposes a cheap substitute for the above-mentioned organic compounds in the form of vegetable materials, more particularly those obtained from straw-like parts of plants with caustic alkali or the like; these materials are certainly somewhat cheaper, but have not as favourable an effect as, for example, glucose.

A further process must be mentioned here which is described in the following patents by R. Linkmeyer, P. Friedrich and the Glanzfäden A.-G., Berlin: British patent 7617/1909, German patent 230,141, Austrian patent 47,147, Swiss patent 48,576, French patent 10,723 (additional to 400,321), and U.S. patent 979,013. This consists in dissolving in cuprammonium solutions parts of plants which contain both cellulose and other carbohydrates, for example rice husks, after they have been disintegrated and decolorized by boiling and bleaching. The process described by R. Hömberg in German patent

237,717, Austrian patent 50,030, and U.S. patent 983,139, according to which aldehydes (with the exception of aldehydic sugars) are added to cuprammonium cellulose solutions, appears to be of very doubtful value, and has acquired no technical importance.

The Soc. An. "Le Crinoid," A. Lecoeur and P. Rudolf, propose to carry out the reduction by the addition of small amounts of formaldehyde. This is said to act at a low temperature, to be cheaper, and also to improve the fibre. (British patent 22,413/1909, French patent 410,827 and U.S. patent 980,294.)

The addition of reducing substances, such as glucose, offers a further advantage; when the alkaline precipitation bath becomes blue during spinning, through the dissolved copper, the threads, which are also blue, cannot readily be observed by the operator, and the breakage of an individual thread can hardly be noticed. The above-mentioned substances, however, particularly on warming, produce by reduction a reddish precipitate of cuprous oxide, by which means the solution is decolorized, so that the blue threads can readily be observed.

Filtration. The spinning solution is carefully filtered before spinning, as described in an earlier chapter, page 73 *et seq.* For the cuprammonium solutions, sand filters were formerly much used, but are now replaced by fine iron or nickel gauze.

According to German patent 410,582, of Hölkenseide G.m.b.H., the filter sieves, filter frames, and all parts of the filter which come into contact with the spinning solution, are easily cleaned by causing the latter to shrink and become detached, by drying at about 60° to 70° C.

THE SPINNING PROCESS

The silk was formerly spun on bobbin machines, which were simply and suitably constructed by Urban on the same principles as those used for collodium silk, and which proved entirely satisfactory, so that they are still largely used with scarcely any modification. (Compare the machines previously described and depicted, page 83 *et seq.*)

For winding, either small bobbins or the rotary glass rollers shown in Fig. 46 were used. The latter had a diameter, for example, of 20 cm., and a length of about 30 cm., whilst the glass was about 10 mm. thick. Reel spinning machines (page 129 *et seq.*) are also used, in which the thread is directly wound

on to reels which, for example, may have a circumference of about 1·2 m., and revolve 25 times per minute.

The continuous process of the Elberfelder Glanzstoffabriken, described on pages 155 and 156, was largely used for cuprammonium silk.

In practice the wet spinning process only has been used for cuprammonium silk. The dry spinning process has been proposed and has been attempted experimentally, but has not so far been adopted in technical practice.

Originally single nozzles of glass, as shown in Fig. 23, were almost exclusively used, and were attached to a glass spinning comb. These have, however, gradually been replaced by multiple nozzles constructed of nickel, which enable spinning to be carried out in an easier and simpler manner.

During spinning, precipitates of copper hydroxide, which interfere with the process, are frequently formed, particularly on the discharge tube of the spinning funnel of stretch-spinning machines (see page 139). A process for the removal of these deposits is described by J. P. Bemberg, A.-G., in German patent 408,889. It consists in periodically introducing a solvent liquid, for example, 10 per cent sulphuric acid, into the stream of precipitating liquid at the point where the deposits occur ; this dissolves the precipitate in the machine. The patent specification shows various forms of apparatus suitable for carrying out the process.

Spinning Baths. Acids, alkalis or salt solutions may be used as spinning baths when spinning cuprammonium silk.

Acid Baths. Originally the spinning bath consisted of 40 to 50 per cent sulphuric acid. In British patent 4303/1901, German patent 125,310, Austrian patent 6150, and U.S. patent 698,254, Bronnert, Fremery, and Urban recommend a spinning bath consisting of 30 to 65 per cent sulphuric acid. According to British patent 4761/1905, French patent 356,402, and U.S. patent 839,013 of Soc. Linkmeyer, a 10 to 20 per cent solution of sulphuric acid is satisfactory if the cuprammonium cellulose solution has previously been freed as far as possible from uncombined ammonia.

The spinning bath proposed by Soc. Anon. " La Soie Nouvelle " in

British patent 9254/1906, French patent 365,057, and U.S. patent 836,620, consists of a mixture of about 37·5 per cent of glycerine sulphuric acid, 25 per cent glycerine and 37·5 per cent water, obtained by carefully mixing glycerine with concentrated sulphuric acid and adding further glycerine. In British patent 18,936/1907, French patent 381,939, and U.S. patent 967,397, A. Lecoeur proposes alkali-bisulphate solutions as a spinning bath. In British patent 11,700/1909, French patent 403,427, Swiss patent 48,335, and U.S. patent 1,062,106, P. Friedrich proposes the use of chlorides of the earths or alkaline earths for the purpose. In German patent 221,041, Hanauer Kunstseidefabrik proposes the use of cold or warm solutions of sulphites, through which gaseous sulphur dioxide may be passed during spinning; and in German patent 222,873, the same firm proposes solutions of ammonium salts, which are alleged to remove both the copper and the ammonia with formation of copper tetrammin salts. In German patent 241,683, Glanzfäden—A.-G., Berlin, proposes a saturated or almost saturated solution of chlorides of the alkaline earths as a spinning bath. In British patent 27,222/1905 of W. P. Dreaper, spinning baths for ammoniacal copper carbonate solutions of cellulose or hydrocellulose are recommended, consisting of solutions of salts, acid salts, or 70 per cent alcohol. A rather remarkable spinning bath is proposed by E. Berenquer in British patent 10,545/1907, consisting of a mixture of 8 kg. of alcohol, 2 kg. of ether, 500 gm. of nitric acid and 8 litres of water.

The alkaline spinning baths described below were preceded by the process described by the Vereinigten Glanzstoffabriken, Elberfeld, in British patent 1283/1905, German patent 169,567, Austrian patent 33,278, French patent 351,208, and U.S. patent 806,533, which is intended primarily for the production of thick threads, and according to which the threads spun in the usual manner in sulphuric acid are wound on a roller which revolves in concentrated caustic soda solution, after which the thread is washed with water or dilute acid and dried under tension. A similar process is used by Gebrüder Übel, Plauen, in the stretch-spinning process. This firm proposes to produce threads by Thiele's process, and to treat them after stretching with strong caustic alkali solution. (See British patent 15,133/1906, German patent 225,161, Austrian patent 37,119, French patent 367,979, and U.S. patent 909,257.) A very similar process of this type is described by R. Linkmeyer in British patent 1501/1905, French patent 350,888, and U.S. patent 839,014.

The acid spinning bath must be used with care and knowledge, as otherwise hard threads possessing but little elasticity are easily obtained. More particularly for the production of artificial horse-hair and similar thick threads the acid spinning bath is not so suitable as the alkaline spinning bath now to be described.

Alkaline Spinning Baths. It should be noted that in this method of spinning cuprammonium cellulose solutions the

ammonia is not fixed by the spinning bath as in the acid process, and that, therefore, measures must be taken to protect the workers from the ammonia vapours which are evolved and for recovering these.

The alkaline spinning bath was first used in 1904. It is successfully used in many cases, including the modern stretch-spinning process. Sodium hydroxide solution is ordinarily used in concentrations varying from highly concentrated to very dilute solutions. The minimum concentration is about 5 per cent of sodium hydroxide, although a solution of about 2·5 per cent concentration is proposed in British patent 4922/1913, German patent 268,261, Austrian patent 67,815, Swiss patent 63,328, French patent 454,811, Belgian patent 254,219, and U.S. patent 1,106,077 of the Vereinigten Glanzstoffabriken. In this case, however, coagulation is assisted by simultaneously using warm concentrated solutions of the salts of oxy-acids.

The temperatures at which alkaline spinning baths are used also vary. R. Linkmeyer (see French patent 347,960) considers that the alkali of the spinning bath acts in a similar manner to that used in the mercerization process. This may be more or less true, more particularly in concentrated baths. The appearance of the thread spun in alkaline solution differs essentially from that spun in acid solution, the latter being milky and turbid, fairly dull, and of light greenish-blue colour, whilst the former is dark blue, transparent, and brilliant.

The thread precipitated in the alkaline bath consists of copper-alkali-cellulose. A portion only of the copper is dissolved in the alkaline bath, to which it imparts an increasingly blue colour in the absence of reducing agents.

The above-mentioned French patent 347,960 of R. Linkmeyer is probably the first in which the alkaline precipitation of cuprammonium silk is referred to. According to British patent 21,988/1904, German patent 186,387, Austrian patent 28,151, French patent 350,220, and U.S. patent 779,175, of the Höchster Farbwerke, subsequently transferred to the Elberfelder Glanzstoffabriken, spinning is carried out in concentrated alkali hydroxide solution, whilst according to German patent of addition 190,217 of the Elberfelder Glanzstoffabriken, dilute solutions are used, containing not less than 5 per cent of the alkaline hydroxide. According to British patent 27,707/1907, German patent 208,472, Austrian patent 35,275, Swiss patent 41,554, French patent

385,083, and U.S. patent 1,030,251, of the latter firm, glucose, saccharose, lactose, or glycerine is added to the concentrated caustic alkali solution, and according to German patent of addition, 218,490, the thread which has been precipitated in an alkaline bath is passed before drying through a bath containing magnesium sulphate, aluminium sulphate, or a similar salt, in order to remove the last traces of alkali.

Other processes of alkaline precipitation are described by Soc. Linkmeyer, in British patent 3549/1906, French patent 361,061, and U.S. patent 857,640 ; by C. R. Linkmeyer in U.S. patent 1,022,097 ; and by Vereinigten Glanzstoffabriken, Elberfeld, in British patent 20,046/1910, German patent 259,816, Austrian patent 60,446, Swiss patent 53,936, and French patent 424,419. According to British patent 22,092/1907, and Austrian patent 35,272 of the latter firm, the thread is spun at a temperature of 45° to 65° C., and according to the same firm's process described in British patent 9268/1908, German patent 229,863, Austrian patent 35,275, French patent 9253 (additional to 385,083) and U.S. patent 1,030,251, the spinning temperature for a bath containing concentrated caustic alkali and glucose or the like, is 45° to 75° C. About the same temperature, namely 40° to 60° C., is recommended by Soc. " La Soie Artificielle " in French patent 379,000, according to which other soluble salts—for example, sodium chloride—are added in order to increase the density of the bath and to facilitate the removal of the copper. Baths containing alkali-hydroxide together with alkali chlorides, are also used in the processes proposed by P. Friedrich and R. Linkmeyer in British patent 17,967/1908, German patent 206,883, Austrian patent 38,809, Swiss patent 40,972, and U.S. patent 962,769. According to French patent 373,429 of C. F. Müller, the precipitation bath consists of a mixture of milk of lime and sodium hydroxide solution. In German patent 248,172, Austrian patent 54,277, and French patent 431,074, R. Pawlikowski uses an aqueous solution of alkali aluminate with or without the addition of free alkali hydroxide.

Apart from the above-mentioned additions to alkaline spinning baths, a number of other additions of various kinds are proposed by various firms or inventors for special purposes. According to German patent 235,366, R. Hömberg uses glue and other colloids. According to German patent 236,297, T. Eck uses methyl-alcohol or a mixture of methyl- and ethyl-alcohols or formaldehyde. According to British patent 11,714/1911, German patent 252,180, Austrian patent 54,428, French patent 440,776, and U.S. patent 1,027,689, the Compagnie Française des Applications de la Cellulose adds arsenites, in order to prevent the solution of a portion of the copper in the spinning bath, and to ensure that the whole of the copper is precipitated within the cellulose fibre. According to British patent 27,878 1910, and French patent 422,565, the same firm recommends the addition of calcium saccharate to the spinning bath. Other additions which are recommended are : diastase, proposed by Legrand in British patent 19,001 1912, German patent 250,357, French patent 445,896, and U.S. patent 1,130,830 ; according to de Haën (British patents 4610 1912 and

11,613/1912, French patent 440,907, and patent of addition 15,861, Belgian patents 243,694, and 245,524 and U.S. patent 1,034,235), nitrites and other reducing substances, such as sodium arsenite, formate, or sulphite, are added to alkaline salt solutions, by which means it is stated that the strength and elasticity of the threads are increased by about 50 per cent. Finally, according to German patent 286,297/1913 of the Glanzfäden A.-G., Berlin, copper carbonate is added, or may be formed in the bath from copper hydroxide and alkali carbonate. We have already referred on page 246 to the bath containing formaldehyde, of the Soc. Anon. " Le Crinoid."

A series of other patents which also deal with alkaline spinning baths for cuprammonium silk are partly very similar to those already mentioned and partly of but little importance. The most important of these are: French patent 383,413 of L. Cuntz; British patent 21,191/1908, French patent 392,869, and patent of addition 9752, of A. Lecoeur and " Le Crinoid " ; British patent 20,316/1908 of Dreaper ; British patent 10 165/1907, German patents 187 696 and 255,549, French patent 377,325 and U.S. patents 839,825 and 1,066,785 of Hanauer Kunstseidefabrik ; and French patent 437.014 of J. Delpech.

Stretch-spinning Process. In the General Section, page 138, we already mentioned the so-called stretch-spinning process as developed more particularly by Edmund Thiele, Rudolf Linkmeyer and J. P. Bemberg, A.-G., Barmen. In all processes of spinning artificial silk a certain degree of stretching of the unconsolidated fibre between the spinning nozzle and the winding machinery had always occurred, but never to more than a fraction of the extent, and more particularly not under the conditions facilitating exceptionally extended stretching, which characterize the stretch-spinning process, and also not with the same exceptional success. The conditions had first to be established under which such considerable stretching of the fibre was possible at all. It was found, more particularly, that the spinning bath in which the first coagulation of the fibre occurred should preferably contain very weak reagents, which only acted slowly on the fibre, so that the latter might remain soft and but slightly fixed, and therefore still be in a condition greatly facilitating stretching.

Two baths were frequently used, the first of which was slow-acting and in which the fibre was formed and stretched, after which it was passed through a second strongly-acting bath. (See, for example, Swiss patent 40,164 of Linkmeyer and Pollak.) For the first bath highly diluted acid could be used,

but it was found that still better results were obtained with solutions which did not form salts with ammonia, that is, with solutions of salts, dilute alkali-hydroxide solutions or organic liquids, such as hydrocarbons or alcohol. For example, A. W. Kracht proposes, in French patent 355,064, that the first bath should consist of concentrated sodium carbonate solution, and the second of concentrated potassium or sodium hydroxide solution. Finally, water was frequently used alone at a definite temperature ; thus, for example, in British patent 8083/1902, German patent 154,507, Austrian patent 21,119, French patent 320,446, and U.S. patent 710,819, Thiele proposes water at 0° to 50° C. as a suitable first spinning bath. In German patent of addition 173,628 and Austrian patent 27,671, he recommends the addition of a small amount of alkali. As a second bath he uses fairly strong acids or more concentrated solutions of alkali-hydroxide.

The reverse principle, namely, the treatment of the thread with spinning baths of decreasing strength, was proposed by Follet and Ditzler in British patent 21,285/1908, German patent 210,280, Austrian patent 43,640, Swiss patent 44,075, and French patent 395,223. According to their process, the fibres are treated, after being discharged from the spinning nozzles, in a number of precipitation baths decreasing in strength, with continued stretching, and are finally washed with pure water. During these processes, the threads are carried over several rollers rotating at varying peripheral speeds, which dip into baths containing the precipitating liquids, and the positions of which, together with those of the precipitation baths, are mutually adjustable, in order to enable the tension of the fibre to be regulated.

P. Friedrich considers it advantageous to combine coagulation and stretching of the fibre in one and the same bath, by forcing spinning solutions of high viscosity into the spinning bath through spinning apertures of 0·35 to 0·45 mm. diameter ; the spinning bath flows through an inclined gutter widened into a funnel at one end, and about 40 cm. long, which feeds an almost horizontal gutter about 1 m. long. The stretching of the fibre is effected partly by the stream of liquid and partly by the pull exerted by the winding bobbin. (See British

patent 28,256/1909, Swiss patent 50,501, Austrian patent 47,777, French patent 407,789, and U.S. patent 1,022,097, which latter is in the name of C. R. Linkmeyer.)

According to British patent 113,010, German patent 303,047, and Swiss patent 75,436 of J. P. Bemberg, A.-G., and E. Elsässer, it is especially advantageous to use as spinning baths for the stretch-spinning process, liquids which are free from dissolved gases. According to German patent 393,947 of Zellstoffverwertungs A.-G. and A. Wagner, the threads discharged from the spinning funnel are treated with iron sulphate solution, by which means it is stated that the individual threads are prevented from adhering, and that a uniform and increased strength of the fibre is obtained.

The stretching of the fibre may be effected by the rotating winding roller. According to British patent 8083/1902, German patent 157,157, French patent 320,446, and U.S. patent 710,819, Thiele utilized the weight of the thread itself, and assisted the stretching process further by the downward current of precipitating liquid. The same principle is applied more intensively in the arrangement described in German patent 220,051/1907 of J. P. Bemberg, A.-G., which has already been described in the General Section, pages 138 and 139, and shown in Fig. 59. (See also German patents 413,790 and 415,798 of the same firm.) An arrangement for carrying out the stretch-spinning process, which is similar in principle, is described in British patent 14,655/1907 of Soc. Linkmeyer, according to which the precipitated thread is carried through a very long tube which is repeatedly bent at right angles. This is, however, a great disadvantage, as it renders the work of the spinning operative much more difficult.

The stretch-spinning process requires more than twice as much sodium-hydroxide as the original process, but only about three-quarters of the quantity of the copper formerly used, and not much more than one-third of the quantity of ammonia used in the original process.

Dry Spinning. General data on the dry spinning process will be found in an earlier section, pages 76 and 77. It has already been mentioned in that section that cuprammonium cellulose

solutions can also be spun by that process, but that generally speaking, such aqueous solutions do not so easily and rapidly form a strong thread in the air as, for example, is the case in the dry spinning process of producing collodium silk, described on page 210 *et seq.* Therefore special methods have been attempted in this case, as for example, by spinning in an atmosphere impregnated with precipitating agents.

In 1904, Soc. Linkmeyer, Brussels, protected a process in German patent 175,296 and Austrian patent 30,449, according to which cuprammonium cellulose solutions containing as little ammonia as possible are spun in an acid or heated gaseous or vaporous atmosphere. According to German patent of addition 185,139, the thread formation takes place in a gaseous atmosphere which is impregnated with a dispersed fog of a substance which precipitates the cellulose. A sort of combined process is described as an alternative in Dreaper's British patent 27,222/1905, according to which the threads are first extruded into the air and are then carried by their own weight into a suitable precipitating bath.

Removal of Copper. Both the alkaline and the acid spinning processes are usually immediately followed, after the removal of adhering traces of the precipitating liquid from the fibre, by a process for the removal of copper. This consists of an exhaustive treatment of the material of the thread with a dilute acid which is usually hydrochloric or sulphuric acid. The process was formerly frequently carried out on the silk whilst still wound on the bobbins. The acid, however, only penetrates with difficulty to the inner layers of thread, and the process therefore requires considerable time and relatively large amounts of acid.

According to British patent 2794/1908, German patent 228,504, French patent 375,827, and U.S. patent 904,684, E. Crumière proposes to immerse the bobbins in dilute acid through which an electric current is passed. The dissolved copper then passes to the cathode, at which it is precipitated and recovered as metallic copper, whilst the acid is continually regenerated. The process is in itself practicable, but requires complicated apparatus, and for this reason and on account of the considerable amount of current required, the process is more expensive than ordinary washing.

The process fairly generally adopted to-day is that of treating the individual fibres with acid, either during spinning or winding (for example, by the use of the thread

gutters described on pages 116 and 117), or the silk is turned in the dilute acid in the usual manner in hank form in wooden vats. The removal of the copper is comparatively rapid, more particularly if thread gutters are used, and with suitable arrangement of the gutters it is possible to restrict the acid requirements to a reasonable amount.

According to British patent 16,088/1906, German patent 179,772, Austrian patent 35,264, and French patent 357,837 of E. Thiele and R. Linkmeyer, a particularly strong lustre, great fineness and soft feel are imparted to the silk by stretching the fibre strongly during souring, that is, during the removal by acids of the copper compound in the fibre spun in an alkaline bath.

Washing. The considerations mentioned in a previous section, page 141 *et seq.*, apply here. If the silk is washed on the bobbins this may conveniently be carried out with the use of the washing stands shown in Figs. 61A and 61B, and by the method of working described in connection with these. In additional patent 111,790 to German patent 111,409 (see also British patent 24,101/1899 and U.S. patent 705,748), the process of the main patent is carried out with the use of acidified or salt-containing water as a washing liquid, after which a short wash with pure water may be carried out if required. According to H. Bernstein's U.S. patent 960,791, the washing of the silk is greatly accelerated by revolving the bobbins on which the thread has been wound in a water bath at 25° to 50° C. The washing water may also be used in the form of steam or as a fine spray.

The further treatment of the silk, that is, the bleaching, drying, doubling, reeling and so forth, is carried out as described on pages 143–155.

According to British patent 6735/1899, German patent 121,429, French patent 286,692, and U.S. patent 691,257 of Fremery and Urban, a very uniform tension of the fibre and a uniform and high lustre are imparted on drying, by carrying out the operation of drying the thread on bobbins or reels with as large a diameter as possible, preferably at a temperature not exceeding 40° C. According to additional patents, British

patent 20,630/1899, German patent 121,430, Austrian patent 11,879, and U.S. patent 650,715, such drying is preceded by treatment with hot water or steam at 70° to 100° C., in order to remove or lessen the adhesion of the water of hydration of the cellulose. It was found that the drying process, as carried out in the main patent, could in this manner be effected in a much shorter time, namely, about one-quarter of the period otherwise necessary. According to French patent 350,889 of R. Linkmeyer and M. Pollak, the threads which are still in a gelatinous condition are stretched by 5 to 20 per cent of their original length, and then dried whilst under this degree of tension. It is stated that threads spun in an alkaline bath are particularly suitable for this process. In British patent 4765/1905, French patent 361,061, and U.S. patent 842,568, R. Linkmeyer states that free ammonia seriously reduces the strength of the fibre in a moist condition, and he therefore proposes to remove this compound immediately after precipitation, for example, by treating the thread, carried on perforated bobbins, in a current of air to remove the ammonia.

Recovery of Chemicals. In the above description of the operation of the various methods of manufacturing cuprammonium silk, reference has been made here and there to the recovery of copper and ammonia. Escaping ammonia vapours are absorbed in water or dilute sulphuric acid. A. Schäfer absorbs ammonia vapours in copper sulphate solution and adds the ammoniacal copper solution so obtained to the main solution. (See Swiss patent 45,321 and U.S. patent 884,298.)

In the stretch-spinning process especially, or when spinning into alkali or water, it is of great advantage to carry out the precipitation in apparatus which is as far as possible closed. From precipitating baths which dissolve the ammonia completely it can be recovered as ammonium sulphate after suitable concentration. The ammonia escaping from alkaline spinning baths can be absorbed as indicated above.

Copper is now recovered by concentrating the copper as far as possible in the acid washing water, and then recovering it as copper sulphate. By this means only about 75 to 80 per cent of the copper can be recovered, but this has, so far, proved

to be the best process. Attempts were frequently made to precipitate the copper as cementation copper by treating the solution with iron turnings. By this means, however, the solution was too much contaminated with iron to be re-utilized in the works without further treatment. Attempts were also made to recover the copper by electrolysis or by precipitation with hydrogen sulphide, but the yields of recovered metal were no greater. Moreover, electrolysis proved to be comparatively expensive on account of the considerable expenditure of current. When precipitating as copper sulphide, great difficulties were usually experienced in filtration.

Soc. Linkmeyer, Brussels, attempt to utilize the well-known power of absorption of cellulose for heavy metal salts for the recovery of copper according to their British patent 3566/1906, German patent 184,150, Austrian patent 35,268, Swiss patent 40,614, French patent 353,187, and U.S. patent 866,371 ; for this purpose cellulose fibre is simply immersed in the copper-bearing spinning bath, and the copper is precipitated on to this, so that the fibres may be directly dissolved in ammonia after further addition of cuprammonium solution. The process, however, gives rise to many difficulties ; the fibres are usually very unevenly impregnated with copper and the recovery is not as complete as might be assumed from the patent specification. The process has, therefore, not been much used. The same remarks apply to the absorption of the dissolved copper by starch or starchy materials as proposed, for example, by L. Cuntz in French patent 383,412 and by the Vereinigten Glanzstoffabriken, Elberfeld, in British patent 27,600/1910, German patent 235,476, French patent 423,104, and U.S. patent 1,049,201. According to British patent 27,539/1910, German patent 239,214, Austrian patent 53,098, French patent 423,064, and U.S. patent 1,023,548, the latter firm proposes to recover ammonia and copper by passing the alkaline washing liquors, containing suspended copper hydroxide, in counter-current to the ammoniacal air, which is aspirated during the precipitation of the cuprammonium cellulose solution. This process is also said to be applicable to acid washing liquors containing copper.

CHAPTER XI

THE PRODUCTION OF VISCOSE SILK

The manufacture of viscose silk is undoubtedly the most interesting artificial silk process from a chemical standpoint. As it is also the cheapest process hitherto employed, it is not surprising that by far the greater portion of artificial silk is to-day produced by this process. The invention on which it is based has already been sketched in the first chapter. It depends on the discovery by the Englishmen, Cross and Bevan, in 1892, that by the action of carbon disulphide on alkali-cellulose the sodium salt of sodium-cellulose-xanthic acid—that is, of a dithiocarbonic acid sodium-cellulose ester—is formed, the aqueous solution of which was called " viscose " by the inventors in allusion to its physical properties.

Cellulose xanthate is obtained in an analogous manner to the alkyl xanthates by the action of carbon disulphide on alkali-cellulose (cellulose-sodium-alcoholate). The first phase of the viscose silk process is, therefore, the production of alkali-cellulose, and is followed by four further main phases. We have, therefore, to distinguish five main processes in the manufacture of viscose silk—

1. Manufacture and ripening of the alkali-cellulose.
2. Production of viscose by treatment of alkali-cellulose with carbon disulphide (xanthation).
3. Ripening of the viscose.
4. Spinning of the viscose.
5. After-treatment of the fibre to produce the finished article.

It is possible to produce viscose in one stage, that is, by the simultaneous action of sodium hydroxide and carbon disulphide on cellulose. This process is, however, not carried out in practice on account of various disadvantages. More particularly, the impurities of the cellulosic raw material which are soluble in alkali, such as wood gum, oxy-cellulose and so forth,

remain as harmful impurities in the viscose when this process is used. Moreover, the advantage is forfeited of being able to regulate the xanthation effect by varying the alkali treatment and so equalizing the irregularities of the raw material. Therefore, pure alkali-cellulose is always first produced. Moreover, the processes are not absolutely identical theoretically in the two cases, for example, with regard to the size of the molecular complexes.

C. C. Leclaire states, however, in French patent 10,929 (additional to French patent 402,804) that he obtains a more uniform product by the simultaneous action of alkali hydroxide and carbon disulphide on wood-pulp. His process has, however, not been applied technically.

ALKALI-CELLULOSE

Theoretical. The chemical nature of alkali-cellulose has been much disputed. It appeared doubtful whether mercerization represented a chemical reaction and whether the reaction product—alkali-cellulose—was, in fact, a chemical compound or the product of an adsorption process ; but Vieweg showed (*Ber.* 1907, page 3876, and 1908, page 3269), and Karrer confirmed (*Cellulosechemie*, 1924, page 69), that although increasing quantities of alkali were absorbed by cellulose with increasing concentration of the caustic alkali solution, the curve representing the quantities of alkali absorbed showed two points of inflexion ; so that within certain limits the quantity of alkali absorbed is constant, independently of the increasing concentration of the solution. Vieweg's table on the absorption of sodium hydroxide by cellulose from solutions of varying concentration, which is given on the next page, shows that the first point of inflexion in the curve lies between sodium hydroxide concentrations of about 16 and 24 per cent, and the second between 35 and 40 per cent.

The quantity of sodium hydroxide absorbed at the first period of constancy, about 13 per cent, corresponds to the proportion of 1 molecule of NaOH per 2 molecules $C_6H_{10}O_5$ or per 1 molecule $C_{12}H_{20}O_{10}$, which is theoretically 12·34 per cent NaOH. This compound was also obtained by Gladstone by

washing mercerized cotton with alcohol. Similarly, the second inflexion of the curve corresponds to the absorption of about 22·5 per cent of NaOH, that is, to the proportion of 2 molecules NaOH to 2 molecules $C_6H_{10}O_5$ or 1 molecule of $C_{12}H_{20}O_{10}$. Such constant molecular proportions of the quantity of alkali are only possible in the case of chemical combination, and not of mere adsorption. Such investigators as E. Heuser (*Cellulosechemie*, 1925, page 13 ; *Zts. angew. Chem.*, 1924, page 1010), K. Hess (*Papierfabr.*, 1925, page 327), and others, therefore assume

Concentration of Solution in gm. NaOH per 100 c.c.	Gm. NaOH per 100 gm. Cellulose
0·4	0·4
2·0	0·9
4·0	2·7
8·0	4·4
12·0	8·4
16·0	12·6
20·0	13·0
24·0	13·0
28·0	15·4
33·0	20·4
35·0	22·6
40·0	22·5

chemical combination to be definitely established. The question whether the alkali combines with the cellulose with the formation of an alcoholate, that is, with the elimination of one molecule of H_2O to form a compound $C_{12}H_{19}O_9ONa$, or whether a mere addition compound is formed corresponding to the formula $C_{12}H_{20}O_{10} \cdot NaOH$ or $(C_6H_{10}O_5)_2 \cdot NaOH$ still remains undecided.

Many reactions of alkali-cellulose undoubtedly belong to the class of alcoholate reactions, such as, for example, the formation of cellulose xanthate by carbon disulphide, of the benzoate with benzoyl chloride, of cellulose-glycollic acid ester with monochloracetic acid, and others. On the other hand, as Heuser points out, the analogy with starch indicates the formation of an additive compound. (See the work of H. Ost

and pupils on wood-pulp, viscose and starch-viscose, in Liebig's *Annalen der Chemie*, 1911, page 340.)

Moreover, alkali-cellulose does not correspond to the above formula in all its stages. According to Vieweg (*Ber. Hauptvers. d. Ver. d. Zellst.-u. Pap.-Chem. u. Ing.*, 1921, page 70), it shows a tendency to polymerization. Whilst the product obtained by dipping cellulose in 18 per cent sodium hydroxide solution corresponds to the formula $(C_6H_{10}O_5)_2 \cdot NaOH$, on pressing the dipped alkali-cellulose compound $(C_6H_{10}O_5)_3 \cdot NaOH$ is said to be produced, and is alleged not to be further altered on action of the alkali for a prolonged period, that is, on ripening the alkali-cellulose.

Production of Alkali-cellulose. *Raw material.* Cotton, for example, in the form of linters (page 30) can be used very successfully for the manufacture of viscose, and is so used by a few firms, especially in America. (See, for example, German patent 381,020.) As described in an earlier chapter (V), the linters are purified with alkalis, bleached, and usually converted into sheets, similarly to wood-pulp. By far the greater part of viscose silk is, however, now manufactured from sulphite pulp, which forms an excellent raw material for the manufacture of viscose silk in the pure and uniform quality in which it is now marketed by various firms.

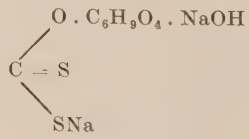
For example, Zellstoffabrik Waldhof, Mannheim-Waldhof, has manufactured for years a special quality of wood-pulp for artificial silk which is specially suited for the purpose, and is in constantly increasing demand by the manufacturers of that product. According to the investigations of the author, this wood-pulp contains up to 89 per cent of pure alpha-cellulose and only very small quantities of wood-gum, resin and ash. This quality is more particularly distinguished by its extraordinary uniformity, which is a property of the greatest importance for the manufacture of viscose.

In German patents 337,672 and patent of addition 344,749, R. Linkmeyer proposes the use of unbleached pulp, which has previously been boiled with acids, for the manufacture of viscose. The main advantage of the process is said to be the low cost of the unbleached cellulose, but this advantage may be

questionable on account of the cost of the acid treatment, the more difficult purification of the mercerizing liquor, and so forth, quite apart from the question whether the process actually readily produces a silk equal in value to that produced from the bleached product. E. Bronnert carries out the acid treatment at an earlier stage by boiling the wood in fragments with highly diluted sulphuric acid before its decomposition, that is, before the sulphite boil. (See German patent 363,997 and Swiss patent 93,302.) This process also has received no practical application.

Hydrocellulose and oxycellulose can also be converted into xanthates, and in German patent 92,590/1896 Cross describes three separate processes for the manufacture of hydrocellulose xanthate. These products are, however, not suitable for the production of artificial silk, as they easily yield threads of low strength.

Proportion of Constituents. As will be clear from the above theoretical considerations, the production of alkali-cellulose is dependent not on the quantity of the sodium hydroxide solution used, but on its concentration. We have seen that for the production of alkali-cellulose corresponding to the formula $(C_6H_{10}O_5)_2 . NaOH$, which, if Vieweg's statements are correct, is converted into $(C_6H_{10}O_5)_3NaOH$ on pressing, a solution is required containing from 16 to 24 per cent of sodium hydroxide. In actual practice a solution containing from 17·5 to 18 per cent is used, but not in the quantities corresponding to the above-mentioned formula for alkali-cellulose, but in considerable excess ; for the calculated quantity of solution will not only be too small for the easy and uniform soaking of the cellulosic raw material, but the formation of xanthate requires further alkali, and the xanthate which is produced is more readily soluble in water in presence of excess of alkali. Cross and Bevan gave to the cellulose-xanthate molecule the formula—



in which there are two sodium atoms to each $C_6H_{10}O_5$ molecule. Although no definite confirmation of this formula has yet been established, it has been found in practice that it is advisable to use the proportions which it indicates, that is, 2 molecules of NaOH per molecule $C_6H_{10}O_5$, or a considerable excess of the former, according to the method adopted.

The method of operation and also the apparatus used for mercerizing vary greatly in various works. Quite generally the cellulosic material is well soaked in excess of 17·5 to 18 per cent sodium hydroxide solution and is freed from excess of the liquid after some time, usually two or three days ; it is then allowed to stand with the absorbed alkaline solution in a heated chamber, the ripening room, in which mercerization is completed, this process being commonly known as the " ripening " of the alkali-cellulose. The process of alkalization occurs quickly and completely in the cold, as was known from the mercerization of cotton. According to Eggert (*Kunststoffe*, 1913, page 382), the best concentration is 18·4 to 18·6 per cent of sodium hydroxide. A contrivance for controlling strength and temperature of the caustic soda solution is described by O. Funke in German patent 412,107. This rather complicated apparatus is, however, unnecessary when reliable operatives are employed.

The treatment with the alkaline liquor can be carried out in various ways ; either vessels with stirrers or so-called disintegrators may be employed. These latter are machines with rapidly revolving sharp-edged stirring blades, resembling in construction and form the Werner-Pfleiderer kneading machines. The cellulosic material, which is torn into large pieces by hand, is thrown through a slot in the cover of the machine, and is caught by the stirring blades and kneaded with the alkaline liquor, which is simultaneously sprayed in through a tube with fine apertures placed above the stirring blades ; the cellulose is thus soaked in the liquor and converted into a thick paste. After interaction for several hours, this is freed from excess of the alkaline solution in a hydraulic press or a centrifuge, and the press-cake so obtained is kept in closed sheet-iron containers in the ripening chamber for about 72

hours at an average temperature of 20° to 25° C. The temperature is determined by the mercerization effect required for the particular cellulosic material, a question which will be discussed later.

According to German patent 408,594 of O. Venter, the disintegrated wood-pulp is soaked with the alkaline solution and repeatedly passed through one or more mixing machines

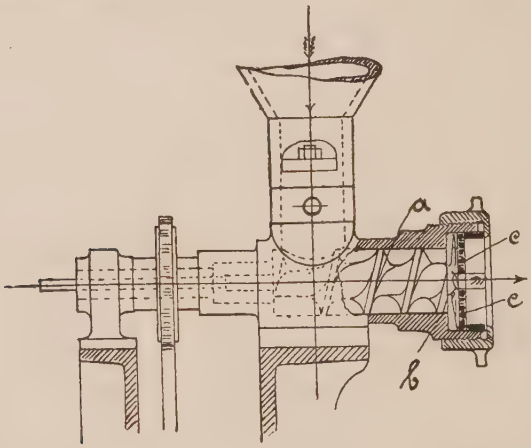


Fig. 84. Venter's Disintegrator for Alkali-cellulose

comprising screw conveyers *a*, cutting knives *b*, and perforated disc-blades *c*, as shown in Fig. 84.

The so-called dipping process is now commonly employed. The cellulosic material, in the form of sheets, is placed in rectangular baskets of wide-meshed wire netting or perforated sheet-iron, in which it is dipped in dipping vats of approximately the same dimensions. Occasionally, no special containers are used, but the sheets of pulp are placed adjacently to one another in the dipping vat, whilst a perforated metal sheet of the same size is interposed after every hundredth sheet. If, for example, the sheets have the dimensions 50 × 50 cm., that is, with an area of $\frac{1}{4}$ sq. m., and the material weighs 400 gm. per sq. m., each sheet will weigh 100 gm., and 1000 sheets comprise a batch of 100 kg. of pulp, so that 10 packs of about 100 boards each are separated by perforated sheets of metal.

After introducing the wood-pulp, caustic soda is introduced into the tank from below, so that the air is displaced upwards and can easily escape. Any air bubbles adhering to the pulp hinder the penetration of the solution, and if necessary, bubbles between the sheets of pulp are removed with the assistance of a flat sheet-iron scraper.

After the action of the alkaline liquor for from 2 to 4 hours, this is withdrawn from the tank and the remaining excess is separated in a hydraulic press, after which the further procedure is as indicated above. By measuring the quantities of liquor withdrawn from the tank and removed by the hydraulic press, the degree of pressure is regulated; that is, the material is pressed to such an extent that the difference between the total quantity of liquor recovered and that initially used—that is, the quantity of liquor remaining in the pulp—corresponds to 2 or $2\frac{1}{2}$ times the quantity of cellulose.

Apparatus has also been constructed in which both the dipping and the pressing are carried out in one operation, and is used in some works. Fig. 85 shows an apparatus, as described in German patent 270,618 of Soc. La Soie Artificielle. A suitable number of sheets are placed vertically between the movable plates *E* and placed with these between the plates *C*. The impregnating liquor is then admitted into the tank *A* in which it acts on the cellulose under suitable conditions. After the completion of the operation the excess of liquor is withdrawn through the opening *K* on the

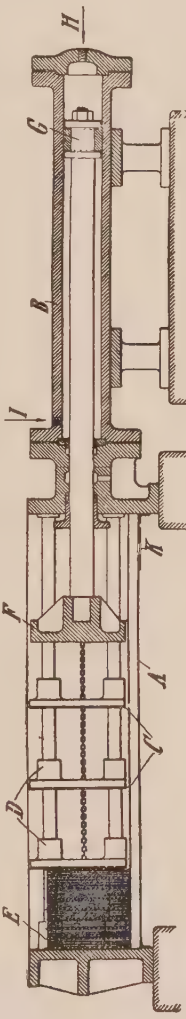


FIG. 85. APPARATUS FOR PREPARING ALKALI-CELLULOSE (*Soc. La Soie Artificielle*)

floor of the tank and the press is actuated until the plates *C* and the pressure head *F* engage with the distance pieces *D*. The arrangement of the press is such as to facilitate the removal of the pressed sheets, after the withdrawal of the piston, in a vertical direction by means of the perforated metal sheets. *H* and *J* are the inlet and outlet ports for the water or other liquid required for actuating the press.

In the apparatus described by F. Kempter in German patent 406,333, the admission and removal of the excess of alkali also take place in the same vessel. This is closed by the pressure head in such a manner that the mass is protected from the action of atmospheric air and also so that no particles of the material may escape the influence of the pressure.

The pressed alkali-cellulose is ground to a crumbly mass in a closed grinding mill or a Werner-Pfleiderer disintegrator. During this process, the alkali-cellulose should not become greasy and pasty, but should form almost dry crumbs. It should be so voluminous and light that 1 litre of the mass should not weigh more than 225 to 235 gm. Should the mass form a compact and more or less slimy paste, 1 litre of which weighs 300 gm. or more, xanthation, filtration and spinning are usually unsatisfactory and the thread is rarely sound. According to Eggert (*Kunststoffe*, 1913, page 382), R. Ohnesorge mentions, as a reaction for sufficient and uniform disintegration, the staining of a sample of the alkali-cellulose with phenol-phthalein followed by the rapid addition of normal sulphuric acid. The red colour should then vanish completely and uniformly in 7 to 8 minutes. In German patent 413,511, the Auergesellschaft describe a process according to which the well-beaten wood-pulp is treated by a continuous process, in which it is cleaned, first with dilute and then with concentrated sodium hydroxide solution, and finally mercerized with an 18 per cent solution. In this case the concentrated mercerizing solution scarcely absorbs any further impurities and can therefore be immediately used for mercerizing further quantities. The removal of the mercerizing liquor as described, by means of centrifuges or on the Foudrinier machine, followed

by pressure rollers, would presumably, however, be accompanied by many difficulties.

The mass of alkali-cellulose is then placed in covered iron containers, which may be portable, in which it is kept for two or three days at an average temperature of 20° to 25° C., according to the required viscosity, in order to ripen. The viscosity of the viscose solution to be obtained from the material depends largely on this ripening process, which must, therefore, be regulated accordingly. The higher the temperature and duration of this process the lower will be the viscosity of the xanthate solution. Probably depolymerization effects in the cellulose complex play the main part in the process. Relatively small temperature changes of 1° to 2° C. are of decisive influence. In order to save time, it is usual to regulate the duration of the ripening process by controlling the temperature. The period would, for example, require to be increased by from 8 to 10 hours in order to obtain the same effect as can be achieved by a temperature rise of 1° to 2° C. Many works utilize an alkali-cellulose which has only been ripened for a short period or at a very low temperature.

It is often assumed that oxidation processes play a part in the ripening of alkali-cellulose, and it has therefore been proposed to utilize the action of fairly strong aeration or the use of oxidizing agents, such as sodium peroxide, hydrogen peroxide, hypochlorite and similar compounds, in order to increase the action, with or without the simultaneous application of a catalyst, for which purpose the oxides or hydroxides of iron, nickel, cobalt, cerium or vanadium are said to be especially suitable. (See Courtaulds, Ltd., German patents 323,784 and 323,785 ; Swiss patents 70,744 and 71,681 ; also Wilson, *J.S.C.I.*, 1920, page 266.) In any case, these communications must be treated with considerable reserve, for alkali-cellulose is in general rather sensitive to the action of the air. Also the carbon dioxide of the air neutralizes the caustic soda and decomposes the cellulose sodium alcoholate ; whilst atmospheric oxygen has an oxidizing influence in presence of alkali and not only acts on the alkali-cellulose as such, but also oxidizes the cellulose molecule. At a raised temperature or on

standing for a considerable period, gradual decomposition occurs, even in the absence of air. Eggert (*loc. cit.*) found the following alterations in the composition of alkali-cellulose after standing for 3 years with complete exclusion of air—

	Initial Composition	Composition after 3 years
Cellulose . . .	24·48 per cent	19·40 per cent
NaOH	15·36 ,, ,,	6·40 ,, ,,
Na_2CO_3 . . .	1·72 ,, ,,	7·95 ,, ,,
H_2O	58·44 ,, ,,	60·25 ,, ,,

The fibre of the alkali-cellulose had been almost completely destroyed, so that under the microscope individual fibre particles could only be distinguished here and there. The viscose obtained from this product showed absolutely no viscosity and could not be converted into a continuous thread.

Other non-oxidizing additions to the alkali-cellulose mixture during mercerization have been proposed in order to facilitate and accelerate the reaction, such as glycerine, alcohol, turkey-red oil, glucose, common salt, carbonates, and so forth, but are probably not used in any works. They offer scarcely any advantage but, on the other hand, they frequently have an unfavourable influence on the xanthation process.

It follows from the considerable influence of small temperature variations, which has already been described, that the temperature of the alkali-cellulose must be constantly and carefully observed during the whole duration of the ripening process. The viscose process is so sensitive in general that it is advisable throughout the whole process to ensure the uniformity of the working conditions as absolutely as possible, and to deviate as little as possible from the average conditions which have once been established as the best, in order to avoid frequent irregularities, bad yield, and other disadvantages. One may, for example, note the small variations which are allowed in practice according to H. Eggert (*loc. cit.*) for the various working conditions: Concentration of the alkaline liquor, 18·4 to 18·6 per cent or 17·5 to 17·7 per cent; pressing to 3·2 to 3·15 times the weight of the cellulose; and so forth.

In various places the treatment with the alkaline liquor has been carried out in edge-runners ; although the impregnation is very intensive and uniform and less liquor is required, this method of operation has the disadvantage that the mass is largely exposed to the prejudicial influence of the atmospheric carbon dioxide, and it is therefore not to be recommended. The alkali-cellulose has occasionally been ground in an edge-runner after dipping and pressing in order to obtain a completely uniform treatment of all the fibres with alkali, but as already indicated closed machines are certainly to be preferred to an edge-runner for this purpose. It should also be noted that provision is often made to maintain the inner temperature of the disintegrator at about 22° to 23° C. by jacketing.

In order further to illustrate these processes we will add a few short practical recipes.

According to Becker (*Die Kunstseide*, page 270), for example, 10 kg. of finely-chopped or disintegrated wood-pulp are intimately mixed in an edge-runner with 30 kg. of 17 to 18 per cent sodium hydroxide solution, which is slowly added, and the alkali-cellulose so prepared is allowed to stand for 48 to 72 hours at the ordinary temperature before treatment with carbon disulphide ; or, according to the same author, one may treat 10 kg. of wood-pulp with 100 kg. of 17 to 18 per cent caustic soda solution in a Werner-Pfleiderer mixer, allow the mass to stand for 24 hours, then press it in a hydraulic press, or treat it in a centrifuge, until the residue is three times the weight of the original wood-pulp, and finally store it for 48 hours in a closed vessel.

The quantity of alkaline liquor given in the last example is very large. A satisfactory alkali-cellulose can be produced in the Werner-Pfleiderer disintegrator when only 40 to 45 kg. of liquor are used per 10 kg. of wood-pulp, after which the mass is pressed until the residue weighs about 30 kg. Too powerful a pressure is in general to be avoided, as it may give rise to a great lack of uniformity in the mass, in consequence of which xanthation does not always occur evenly, and the viscose may contain cellulose particles which are either imperfectly attacked or unattacked.

In general, treatment in a centrifuge is to be preferred to pressing, as it yields a more even product. When the press is used the centres of the sheets are usually more strongly pressed than the edges, but in large works pressing is a necessity, as the output of the centrifuges is too small.

By the above described methods alkali-cellulose is obtained as a press-cake containing about 25 per cent of cellulose and 75 per cent of liquor.

These proportions can be deduced as follows: as the wood pulp contains on an average 12 per cent of substances soluble in alkali and 12 per cent moisture, the 10 kg. of dry pulp which are used contain only 7·6 kg. of pure cellulose, 1·2 kg. of substances soluble in alkali, and 1·2 kg. of water. If this 10 kg. of pulp are treated with 45 kg. of 18 per cent caustic soda solution, and 25 kg. of liquor are removed by pressure from the total mass, which weighs 55 kg., a press-cake is obtained weighing 30 kg., and the expressed liquor contains 1·2 kg. of substances soluble in alkali (from the wood-pulp) and 23·8 kg. of liquor, whilst the press-cake, of a total weight of 30 kg., contains 7·6 kg. pure cellulose, equal to 25 per cent, and 22·4 kg. of liquor, equal to 75 per cent. The concentration of the liquor is also appreciably reduced.

According to Eggert (*loc. cit.*) a satisfactory alkali-cellulose should have the following composition: Cellulose, 26 to 27 per cent; NaOH, 15 to 16 per cent; Na_2CO_3, 0·3 to 1·0 per cent.

Disintegrators of larger dimensions are also constructed in which 30 kg. and more of wood-pulp can be treated in one batch.

In German patents 352,962 and 353,948, C. L. Stulmeyer recommends, for the purpose of ensuring intimate admixture of the wood-pulp, that the alkali within the container should be strongly evacuated during the reaction, after which the mass may with advantage be exposed to more than atmospheric pressure.

F. Beltzer (*Kunststoffe*, 1912, page 41), describes a process in which moist wood-pulp, containing 50 per cent of water, is used. The alkaline liquor must then naturally be used of correspondingly increased concentration. To 100 kg. of this pulp about 50 litres of caustic soda solution of 40° Bé. (35 per cent NaOH) are gradually added in a thin stream in an edge-runner until the ground mass is absolutely evenly impregnated.

F. Erban (*Kunststoffe*, 1911, page 168) supplies the following recipe: For the manufacture of viscose a cellulosic material is used which has been ground in a pulp-engine to 2 mm. length of fibre and has been centrifuged to 50 per cent water contents. For each 2 parts of dry cellulose 1 part of solid caustic soda is used, which is dissolved in 4 to 6 parts of water. The treatment is carried out either in an edge-runner, in which the cellulose is ground with slow addition of the alkaline liquor, or the cellulose is mixed with 10 times its weight of 18 per cent alkali in a mixing and kneading machine, and allowed to drain for $\frac{1}{4}$ to 1 hour. It is then centrifuged and ground, after which, in either case, it is pressed through a sieve of 6 mm. mesh, cooled and stored in closed barrels so that too much carbon dioxide shall not be absorbed. At 10° to 15° C. the product is said to be still utilizable after 10 days, but at 20° to 30° C., after 3 days at the utmost. The proportion of carbonate must not exceed 5 per cent of the total alkali. Alkali-cellulose which has been decomposed by long storage in a warm place or by contact with the air, yields a freely-flowing viscose, which forms a very brittle cellulose.

Recovery of Alkali. A small portion of the alkaline liquor removed from the alkali-cellulose by pressing can be directly used in new batches. Hitherto no practical and cheap process of freeing the alkaline liquor obtained in the press from hemicelluloses, resins and other impurities has been devised, by which it could be rendered completely suitable for a further mercerizing process. A number of processes have been proposed for the purpose, but the problem has in no sense been solved.

The most obvious method of evaporating, calcining, and causticizing the liquor, requires heat in too large a quantity, and is, therefore, too expensive. In British patent 1573/1912, German patent 252,179, Swiss patent 58,424, and French patent 449,457, Soc. La Soie Artificielle propose to treat the waste liquors at a suitable concentration and temperature with the salts of heavy metals, preferably with copper compounds, by which means the hemicelluloses and other cellulose derivatives are precipitated as copper-sodium-cellulose compounds. In order not to contaminate the solution with the salts of

heavy metals, it is preferable to stir it with the experimentally determined quantity of freshly-precipitated cupric hydroxide, which has been washed by decantation, for some hours with access of air. The process has been applied on a manufacturing scale, but apparently it is very difficult to obtain the alkaline solution quite free from traces of copper, which impart a dark colour to the viscose through the formation of copper sulphide, and cause the thread obtained on spinning to have a greenish-grey colour, which is difficult to remove. German patent 406,497 of the Vereinigten Glanzstoffabriken, Elberfeld, Mönkemeyer and Zart describes a process for the treatment of the copper-bearing precipitate. According to German patent 287,092, F. Küttner purifies the waste liquors by dialysis with water or pure dilute caustic alkali. It is true that the hemicelluloses, being colloids, are mainly retained by the dialyzing membrane, through which the alkali diffuses, but the process is impossible in practice as, generally speaking, relatively small amounts of liquid only can be treated by dialytic processes, and very high dilutions are obtained. Moreover, the process requires complicated apparatus, and very slight accidents—such, for example, as small leaks in the membrane—nullify the results. In a further patent, German patent 355,836, the same inventor proposes another method, namely the removal of the organic substances from the liquor without warming, by the use of an oxidizing agent, such as H_2O_2, in presence of catalysts, such as copper, lead, and so forth.

PREPARATION OF VISCOSE (XANTHATION)

Theoretical. If we bear in mind that ordinary ethyl alcohol, for example, reacts with sodium to form sodium-alcoholate, C_2H_5ONa, and that this reacts with carbon disulphide according to the equation

$$C_2H_5ONa + CS_2 = SC(SNa)(OC_2H_5)$$

to form a sodium salt of a xanthic acid—which in this case is ethyl-xanthic acid—it is quite comprehensible that cellulose which is also an alcohol in virtue of its free hydroxyl groups and which reacts chemically with sodium hydroxide as shown

in the previous section, is also capable of forming the sodium salt of a cellulose xanthic acid.

We may interpose here a few remarks on chemical nomenclature, which is often confused in the literature and elsewhere. The description " xanthic acid ester " is incorrect, for the term " xanthic acid " already implies the esterification of the hydroxyl group, as xanthic acids are acid esters of the general formula RO · CS · SH (in which R represents any alcohol radical), that is, esters of a dithiocarbonic acid or, more definitely, of sulphthiocarbonic acid, SC(SH) (OH), as distinct from ordinary dithiocarbonic acid, $CO(SH)_2$. According to the alcohol which is esterified, one speaks of " methyl-xanthic acid," " ethyl-xanthic acid," and so forth. In our case, in which cellulose plays the part of an alcohol, the description " cellulose-xanthic acid " is correct, and its sodium salt should be described as " cellulose-xanthate " or " cellulose-sodium-xanthate."

According to Cross and Bevan, the esterified cellulose residue in viscose is also combined with alkali ; on this view the compound is the sodium salt of a sodium-cellulose-xanthic acid, namely " sodium-cellulose-xanthate," which may also be described as " sodium-cellulose-sodium-xanthate," " sodium-cellulose-dithiocarbonate " or " sulphthiocarbonate " or as the sodium salt of sodium-cellulose sulphthiocarbonic acid.

It may be mentioned here that starch, which is allied to cellulose, forms a similar xanthate, to which Ost gives the formula

$$NaS \cdot C \cdot S\,(OC_6H_8O_3Na)$$

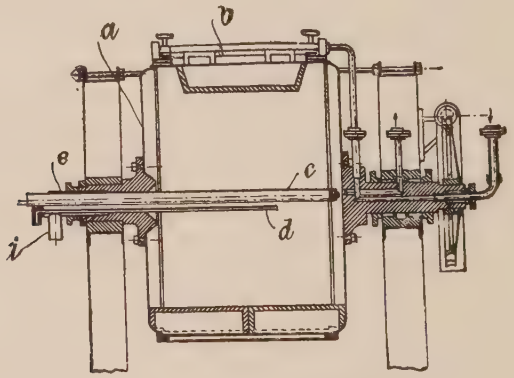
In accordance with the above equation for the formation of ethyl-xanthate, the formation of cellulose-xanthate is usually formulated as follows—

$$C_6H_9O_4 \cdot ONa + CS_2 = \begin{matrix} O(C_6H_9O_4) \\ | \\ C \cdot SNa \\ \| \\ S \end{matrix}$$

This equation, however, certainly does not correspond to all details of the actual process. In the previous section, pages 259 and 260, we have already seen that the alkali-cellulose molecule does not correspond to the formula $C_6H_9O_4 \cdot ONa$, but to $(C_6H_{10}O_5)_2 \cdot NaOH$, or, according to Vieweg's statements, after pressing, to the formula $(C_6H_{10}O_5)_3 \cdot NaOH$. Moreover, in the initial stages, alkali-cellulose xanthate certainly has not the formula given in the preceding equation, a subject to which we will return in a later page, on the Ripening of Viscose. We may further mention here that the

statements of Burette, in French patent 430,221, that 15 to 20 per cent of carbon disulphide, calculated on the weight of cellulose, suffices for xanthation, led Vieweg to the conclusion (*Ber. Hauptvers Ver. d. Zellst. u. Pap. Chem.*, 1921, page 72), that in its first stage cellulose-xanthate corresponds to the formula $(C_6H_{10}O_5)_3 . CS_2 . NaOH$. This formula cannot, however, be considered to be proved, as apparently the statements of the above-mentioned French patent still require confirmation.

Operation of the Xanthation Process. The treatment of alkali-cellulose with carbon disulphide was formerly carried



(*Herminghaus & Co.*)

FIG. 86. XANTHATION DRUM

out in long cylindrical or polyhedric wooden containers or mixers, which revolved about a horizontal axis. To-day, either Werner-Pfleiderer mixers of iron are used, which may be internally nickel-plated or lined with nickel plates, or simple iron xanthation churns, rotating about a horizontal axis. The machines are provided with a jacket through which cold or warm water can be circulated. In some works, small xanthation units are preferred, in which the individual batches of alkali-cellulose are separately treated. In other works, large xanthation installations are employed and several batches of alkali-cellulose are simultaneously treated. In some works the alkali-cellulose is exposed to a vacuum in the xanthation plant in order to remove the air as far as possible before the

carbon disulphide is added, for the purpose of enabling this latter compound to act more readily. (See German patent 322,047 of P. Joliots.)

Fig. 86 shows a xanthation churn described in German patent 375,712 of Herminghaus & Co., which is used for a xanthation process in which the air is expelled from the mixing drums with the help of carbon dioxide, nitrogen, or any other suitable gas for the replacement or dilution of the oxygen ; in this apparatus the carbon disulphide vapours are also removed after xanthation with the aid of a gas, which is aspirated or expelled by pressure from the container. In Fig. 86, *a* is the mixing drum with a cover *b* ; *c* is a supply pipe for the gas (nitrogen or carbon dioxide) ; *d* is the supply pipe for the carbon disulphide. Both pipes are carried through the stuffing box *e* ; *i* is a connection for the pipe leading to the vacuum pump.

The quantity of carbon disulphide used varies from one works to another. Formerly, 1 molecule of carbon disulphide was used per molecule of cellulose ; that is, 60 kg. CS_2 per 100 kg. of wood-pulp. This quantity is mentioned by Becker (*loc. cit.*, page 270), also by Beltzer (*loc. cit.*, page 45). Smaller quantities may, however, be used. According to French patent 430,221, 16 kg. of CS_2 suffice for 100 kg. of cellulose, as already mentioned ; these proportions would correspond to 1 molecule of CS_2 only per 3 molecules of cellulose, and would, therefore, correspond to the formula $(C_6H_{10}O_5)_3CS_2 \,.\, NaOH$. It is, however, clear from the patent just cited that such small amounts of carbon disulphide can only be used under quite exceptional working conditions. It should also be borne in mind that an appreciable portion of the carbon disulphide is lost through inevitable by-reactions.

By-reactions. These are numerous. More especially, sodium trithiocarbonate is produced, together with carbonate, by the action of the alkali in the viscose, according to the equation—

$$3CS_2 + 6NaOH = Na_2CO_3 + 2Na_2CS_3 + 3H_2O$$

Sodium sulphide is readily formed in the solution, and reacts with carbon disulphide with formation of trithiocarbonate—

$$Na_2S + CS_2 = Na_2CS_3$$

Sodium trithiocarbonate is a salt very readily soluble in water, which is precipitated from its aqueous solutions by alcohol in the form of a red oil, which only crystallizes to a brownish-yellow crystalline mass at fairly high concentrations. The intense reddish-yellow colour of viscose is partly due to this salt and largely due to the polysulphides, which are also present in considerable amount; it is not due to the cellulose-xanthate itself. Dilute aqueous solutions of this salt rapidly absorb oxygen from the air, and decompose with separation of sulphur and formation of carbonate according to the equation—

$$Na_2CS_3 + 3O = Na_2CO_3 + 3S$$

On boiling, the aqueous solution evolves hydrogen sulphide according to the equation—

$$Na_2CS_3 + 3H_2O = Na_2CO_3 + 3H_2S$$

Naturally, hydrogen sulphide immediately reacts with the alkali of the viscose to form sulphide. Simultaneously polysulphides are produced, partly by oxidation of sulphides, according to the equation—

$$5Na_2S + 4O + 4H_2O = Na_2S_5 + 8NaOH$$

partly by the solution of sulphur, which is produced by the decomposition of the trithionate (see above equation), and also by the oxidation of H_2S. The aqueous solutions of polysulphides are also deep reddish-brown in colour, or more or less orange yellow, according to their concentration. They have an odour of hydrogen sulphide.

During xanthation, the *temperature* is not allowed to rise above 25° to 30° C. Water-cooling is, therefore, used if necessary, and for this purpose the apparatus is enclosed in a water jacket, as already mentioned. The process is accelerated by rise of temperature, but a better xanthate is obtained if xanthation takes place rather more slowly at a lower temperature.

The time required for xanthation is from 3 to 4 hours, and the process is finished when a sample of the xanthate dissolves in water to a clear solution free from fibres. The mass then has a dark reddish-yellow to brownish-yellow colour, has lost its crumbly consistency, and forms a tough paste which appears to be homogeneous. Exact investigation shows that the fibrous structure has been more or less maintained, and only vanishes during the solution which follows xanthation.

The excess of carbon disulphide is removed from the apparatus by an air current, which is blown or aspirated through the continuously stirred mass before the solution process. Solution is often carried out in the actual xanthation churn,

either completely or up to a certain point, in which latter case the viscose from the apparatus is further diluted in the solution tank. Frequently, however, the undiluted xanthate is transferred to the solution tanks in order to save time for the next xanthation, and is dissolved in the tank. Viscose solutions are usually adjusted so that they may contain 6 to 8 per cent of cellulose and about 8 per cent of caustic soda. For this purpose about 50 kg. of caustic soda and 565 kg. of water must be added to a batch obtained from 100 kg. of wood-pulp.

These data may be deduced as follows : We may assume that 100 kg. of air-dried wood-pulp contain 76 kg. of pure cellulose. As these 76 kg. are to be obtained in the form of a 7 per cent solution, they must be dissolved to form 1085 kg. of solution. These 1085 kg. contain 300 kg. of alkali-cellulose and 60 kg. of carbon disulphide, and consequently 615 kg. of solvent has to be added. The composition of this solvent can be calculated from the requirements that the viscose shall contain 8 per cent of NaOH, that is, 87 kg. NaOH in all. The 300 kg. of alkali-cellulose contain 25 per cent, that is 75 kg. of pure cellulose, and 75 per cent, equal to 225 kg., of caustic liquor, with about 37 kg. of NaOH, in addition : Therefore 87 – 37 kg. = 50 kg. of NaOH, must be added ; consequently, 50 kg. NaOH, and 615 – 50 = 565 kg. of water, must be added for solution, for which purpose 337 kg. of water, and 278 kg. of 18 per cent caustic soda solution, may be used.

The mass is well stirred and the solvent added very slowly at first, which causes solution to occur more quickly and uniformly ; the remainder may then be added as rapidly as desired. In some cases the operation is reversed, and the dilute alkaline liquor is first placed in the container and the xanthate slowly added from the xanthation drum.

In common with all spinning solutions, viscose must be very carefully filtered and de-aerated, as described in the earlier section, pages 73 and 74. Viscose is filtered in the same manner as collodium, in a filter press, the chambers of which are lined with cotton-wool. In order to hold it together the cotton-wool is usually held between wide-meshed cotton gauze. De-aeration is usually carried out, at any rate partially, simultaneously with the ripening process.

After filtration, the viscose passes to the ripening chamber. Before considering the ripening process we will briefly review the most important properties of viscose.

Properties of Viscose. Viscose is a viscous, oily, brownish-yellow to yellowish-red solution of characteristic odour, which is essentially different from that of hydrogen sulphide, although the odour of the latter substance is definitely present, particularly in the case of ripened viscose solutions. The degree of viscosity of the solution depends on the concentration, and also on the nature and previous treatment of the cellulosic material. When discussing alkali-cellulose we have already mentioned that the viscosity of the xanthate solution is lower, the longer the duration of the ripening process and the higher the ripening temperature of the alkali-cellulose.

Mineral acids decompose both the sulphur-containing by-products, mentioned in the previous Section, and cellulose-xanthate itself, the latter re-forming cellulose in the form of cellulose hydrate, which possesses the chemical composition of pure cellulose. Mineral acids are therefore used in the manufacture of viscose silk for the production of the cellulose fibre from viscose, either by direct spinning in a mineral acid bath or by subsequent fixation of the thread which has previously been precipitated in the form of xanthate. In agreement with the above-mentioned considerations, considerable quantities of hydrogen sulphide are liberated during this decomposition. Carbon dioxide precipitates the xanthate as such, whilst sulphur dioxide effects no precipitation nor decomposition.

Organic acids, such as formic, acetic, oxalic and lactic acids, behave quite differently. They decompose the by-products only, but not the cellulose xanthate itself, which is separated essentially unchanged in a comparatively pure condition, and can then be re-dissolved after separation from the mother liquor, a process which is utilized for purifying viscose.

Alkali salts and ammonium salts can be used in the same manner, as they also precipitate the unchanged xanthate. According to Margosches (*Die Viscose*, 1906, page 75), when ammonium salts are used the sodium in the xanthate is replaced by ammonium. For further particulars, see the section on Purified Viscose, later (page 280 *et seq.*).

Zinc salts and all salts of heavy metals give variously-coloured precipitates of metallic xanthates with viscose solution.

According to Margosches, the zinc xanthate precipitated by zinc salts forms horny white flocks which are soluble in alkali. Various salts of heavy metals form characteristically-coloured precipitates, which are coloured as follows, according to the communication of Seidel (*Mitt. K. K. Techn. Gewerbemuseum*, 1900, page 35): Iron, brownish-red ; lead, carmine red ; mercury, yellow ; bismuth, reddish-brown ; copper, chocolate-brown ; nickel, cherry-red. Haller (*Zts. Farben-u. Text.-Ind.*, 1904, page 81 *et seq.*), describes tin xanthate as a dark reddish-brown precipitate. Wolffenstein and Öser (*Kunstseide*, 1925, page 29), describe the colour of the mercury compound as brownish-black (possibly in consequence of admixed mercury sulphide), that of the tin compound as dark yellow, and the colours of xanthates obtained with other metallic salts as follows: Cobalt, brownish-black ; silver, rust-brown ; cadmium, yellow ; antimony, reddish-yellow. Although Seidel ascribes the colorations to the admixture of thiocarbonates, as the precipitates are lighter and less intensively coloured the more carefully the viscose has been purified, Margosches (*loc. cit.*) considers the coloured precipitates to be characteristic for the respective metallic compounds. It is stated that by means of the nickel salt the conversion of alkali-cellulose into xanthate during the production of viscose can be followed step by step.

The reaction of cellulose xanthate with iodine was discovered by Cross and Bevan, the inventors of viscose. They consider the precipitated flocculent product of the reaction to be cellulose-dihydroxy-thiocarbonate, and they formulate the reaction as follows—

$$CS\begin{matrix}OX\\SNa\end{matrix} + \begin{matrix}XO\\NaS\end{matrix}CS + I_2 = 2NaI + CS\begin{matrix}OX & XO\\S\text{——}S\end{matrix}CS$$

The precipitate dissolves in alkalis in presence of a reducing agent with re-formation of the xanthate.

The equations for this reaction vary according to the degree of ripeness of the viscose, as the required quantity of iodine depends on the quantity of combined alkali, which varies in turn with the degree of ripeness. Attempts have therefore

been made to utilize this reaction for the determination of the degree of ripeness. (For further details see pages 284 and 285 in the section on the Ripening of Viscose.) L. Vignon (*Bull. Soc. Chim.*, 1904, page 105 ; *Chem. Zentr.*, 1904, I, page 651), investigated the optical activity, not only of cellulose and cellulose nitrates, but also of viscose, and thinks he observed a slight rotation to the right. He did not succeed, however, in obtaining solutions sufficiently clear to enable him to make reliable determinations of the degree of rotation.

The stability of cellulose-xanthate solution is relatively small. At the ordinary temperature, and even when strongly cooled, and when all external influences are eliminated, a decomposition gradually occurs, which can be followed by the change in the physical properties, such as viscosity, rapidity of coagulation, and so forth. Warming very greatly accelerates the process of decomposition According to Cross and Bevan viscose can be kept for about 14 days at temperatures below 10° C., and for 6 to 10 days only between 10° and 20° C. Concentrated solutions decompose more rapidly than dilute solutions, and those containing but little alkali more rapidly than those with a large excess of alkali. The presence of salts also influences the process very considerably ; by the addition of very small quantities of acid or salt the decomposition is accelerated. The carbon dioxide of the atmosphere also acts in the same manner if it is allowed free access to viscose solution. On the other hand, the addition of alkali retards the decomposition, and may even reverse the process to a certain extent.

During this process of decomposition, cellulose xanthate passes through a number of definite phases, which will be discussed in detail in the section found on page 283. The stage which has been attained by this process of decomposition—which is technically known as " ripening " of the viscose—is a by no means unimportant factor in the production of the fibre.

Purified Viscose. When describing the properties of viscose, we noted that weak acids, such as formic, acetic and carbonic acids, and various other precipitants, such as salts, alcohol and so forth, precipitate the xanthate from the viscose

solution in an unchanged condition, that is, without decomposition. As the by-products, and more particularly the various sulphur-alkali compounds, are soluble in solutions of these precipitants, or are decomposed by them in so far as they are of acid character, this process can be utilized in order to obtain viscose almost free from by-products. For this purpose viscose solution is precipitated with one of the above-mentioned reagents, or preferably with a mixture of one of the above-mentioned acids and a salt, and washed with the same solution until all the by-products have been removed as completely as possible. The crumbly, more or less yellowish-brown mass which is so obtained is then re-dissolved in dilute sodium hydroxide solution. A process of purification of this kind is described, for example, in German patent 133,144 of the Viscose Syndicate, London. The coagulation of viscose by warming to about 50° C., followed by washing with salt solution and re-solution, has similarly been used for its purification. (See German patent 187,369 and French patent 334,636 of the Soc. de la Viscose.) According to German patent 209,161 of the Continental Viscose Co., carbon dioxide is used as a precipitant for purification. The Vereinigten Kunstseidefabriken A.-G., Kelsterbach, claim that they obtain a relatively pure cellulose xanthate by acting on the non-coagulated viscose solution with aluminium or chromium salts. It is stated that by this means the sulphide compounds are removed by interacting with the salts of the heavy metals, and that on standing the cellulose xanthate separates in a very pure condition, and is washed in the usual manner and re-dissolved in alkali. (See British patent 8742/1908, German patent 200,023, Austrian patent 37,137, and French patent 389,284.) According to German patent 197,086, J. P. Bemberg, A.-G. purify viscose by treating it with an aqueous solution of sulphurous acid or bisulphite until the viscose shrinks and becomes hard. It is then pressed and washed with dilute bisulphite solution. According to British patent 8023/1908 and German patent 237,261, L. Lynke purifies viscose by precipitation with methyl- or ethyl-alcohol. According to German patent 228,836 and U.S. patent 980,648, L. Lilienfeld obtains a xanthate which

keeps well in the dry condition and is soluble in alkalis and sometimes even in water, by treating the crude or purified xanthate in solution with oxidizing agents (potassium manganate or permanganate) and then precipitating. According to British patent 14,339/1914, German patent 323,891, and French patent 474,793, the same inventor obtains a "polymerized xanthate" by warming for a short period at 60° to 80° C.; the product is insoluble in water and soluble in dilute alkalis, and its solutions are said to be distinguished by great stability, and may, for example, be allowed to stand for several weeks at the ordinary temperature without coagulation. According to German patent 234,861, F. Becker purifies crude viscose by dialysis, probably in imitation of the application of the same process to collodium and cuprammonium silk. In all these cases the process is not technically possible. Dialysis requires much time, and by its means it is impossible to treat large quantities of solution without an excessively large plant. Moreover, the viscose has to be much too strongly diluted, and finally, the stabilizing element, the alkali, is removed together with the impurities, causing the viscose immediately to coagulate unless the alkali is continuously replaced, which would be much too dear. A. Bernstein proposes to purify viscose without precipitation of the xanthate, in U.S. patent 1,121,605, Belgian patent 259,495, and French patent 462,147. After xanthation has been completed he conveys the xanthate into a vertical container with a conical floor, provided with a sieve, discharging cock and stirrer, and washes it for some minutes by stirring with water to which a small amount of acid (acetic acid) has been added. On opening the discharge cock a reddish liquid is said to be discharged, which contains the greater portion of the injurious sulphur-bearing by-products. The excess of carbon disulphide, which is condensed by cold water, is said to be simultaneously discharged. The process could probably not be carried out during continuous manufacture. Whilst still unripe, viscose dissolves, as we have already seen, in dilute acetic acid solution, and therefore if the washing water contains but little acid it will dissolve xanthate; if, however, it contains too much acid it will cause precipitation

According to German patent 408,822, the Auer-Gesellschaft frees viscose from injurious metallic oxides, and more particularly from the alkaline earth oxides, by adding substances which form, with the oxides in question, compounds which are insoluble in strongly-alkaline solutions ; such additions are boric acid, phosphoric acid or their soluble salts, or the like. The precipitated insoluble compounds produced are to be removed by filtration.

All these processes of purification, with the possible exception of the last-mentioned, are, however, only used in cases where the contaminating by-products would cause the viscose to be useless. It has been found that such a purification is superfluous for the production of artificial silk, and it is probably never used practically, as it would only complicate the whole process and make it more expensive.

THE RIPENING OF VISCOSE

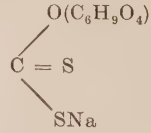
Cellulose xanthate is a colloid, and viscose is a colloidal solution. The ripening of viscose is a colloid-chemical process, the underlying causes of which are to be found in chemical changes of the molecular complex. If we bear in mind that the xanthic acid radical is the soluble component of the viscose molecule and the cellulose radical a component which is itself insoluble and which only becomes soluble by virtue of the combination, it is obvious that as the proportion of the cellulose compound in the molecule increases the solubility of the compound will steadily decrease until finally, when the proportion of cellulose has attained 100 per cent (a condition which is attained when it has been converted into cellulose hydrate by the elimination of all the xanthic acid residues) it becomes completely insoluble. When this stage is attained the viscose coagulates with precipitation of cellulose hydrate. When passing through all the previous stages, however, the viscose passes through all the properties which might be expected in view of the steadily-decreasing solubility ; for the smaller the solubility of the compound the greater will be its viscosity at constant concentration, and the more rapidly will it coagulate on addition of a precipitating agent and the less of such

coagulating agent will be necessary in order to coagulate the solution, and so forth ; all these phenomena are actually shown by viscose during the ripening process.

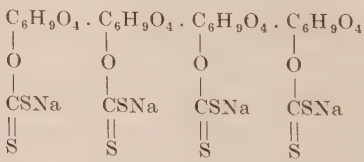
The fact that in the course of the ripening process the proportion of cellulose in the molecule increases and the proportion of xanthic acid residues decreases can be chemically proved by determination of the relative proportions of sulphur and of sodium to cellulose. If this determination is carried out during several days in the case of a normal spinning viscose containing about 7 per cent of cellulose, and which is kept at a temperature of about 20° C., approximately the following average figures will be obtained—

	Sodium	Sulphur	Cellulose
1st Day	1	2	1
2nd ,, ...	1	2	2
5th ,, ...	1	2	3
7th ,, ...	1	2	4
9th ,, ...	Product separated consisting of cellulose only.		

We may therefore visualize the ripening process as follows: Initially, at least 4 molecules of

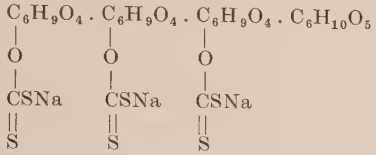


are combined to a molecular complex, possibly as follows—

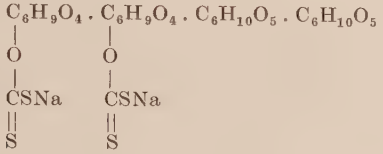


We may then assume that during the course of ripening xanthic acid residues are eliminated, and the compound passes through the following stages—

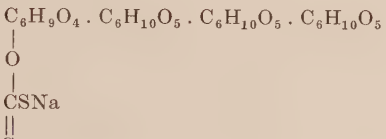
On the second day:



On the fifth day:



On the seventh day:



On the ninth day:

This is, of course, merely a scheme which represents the process broadly, for it must not be assumed that these formulae correspond to the actual conditions in all details; more particularly, the molecular weight of the complex is at present quite unknown. We have also seen in the previous section that the formula of alkali-cellulose is by no means yet established with certainty.

In accordance with the preceding formulae, the proportion of combined xanthate-alkali decreases steadily during the ripening, a process which it has been attempted to utilize for the determination of the degree of ripening (for details regarding this matter see pages 287 and 288).

For most spinning processes the optimum condition for the spinning of viscose is that in which it has the composition as described above for the seventh day. At this stage the velocity

of coagulation of the viscose is so high that in contact with the coagulating agent (spinning bath) thread formation occurs immediately. C. H. Stearn (British patent 7,023/1903, U.S. patent 716,778, and French patent 330,753), realized the essential nature of the ripening process, and his formulae for the various stages of ripening represent the correct proportions. He merely gives the proportion of cellulose residue combined with one xanthate residue in each case, and so obtains the series of formulae $C_6H_9O_5CS_2Na$; $C_{12}H_{19}O_{10}CS_2Na$; $C_{18}H_{29}O_{15}CS_2Na$; $C_{24}H_{39}O_{20}CS_2Na$, and so forth. Stearn also investigated the solubility conditions at the various stages. The original (C_6) compound is readily soluble without decomposition in water, brine, sodium hydroxide solution, acetic acid and lactic acid. The C_{12}-compound is soluble in water sodium hydroxide solution and dilute acids, but is converted by brine into a gelatinous mass. The C_{24}-compound is insoluble in water and in the above-mentioned acids, but dissolves in sodium hydroxide solution of suitable concentration.

Determination of the Degree of Ripeness. The process just described affords a method of determining the degree of ripeness of viscose ; for example, a sample of the viscose is poured in a thin stream into dilute formic or acetic acid (of about 10 per cent concentration) and stirred with a glass rod. If the viscose dissolves completely it is still unripe. A larger or smaller quantity of insoluble flocks shows a somewhat higher degree of ripeness. If, however, the viscose forms an insoluble, continuous thread which does not dissolve on further stirring but remains solid, the necessary degree of ripeness has been attained, and has been the more completely attained the more easily the formation of thread takes place, and the more compactly the thread holds together. With a little practice the optimum spinning condition can be approximately determined. This remains, however, an inexact method, which is merely useful as a rough preliminary test in the works.

The degree of ripeness can be very exactly determined by Hottenroth's method (*Chem. Ztg.*, 1915, page 119). Hottenroth found that the speed of coagulation of the solution increases with the degree of ripeness, and that, for example, a ripe

viscose coagulates in a far shorter time with a definite quantity of acid than an unripe viscose, and that, correspondingly, a riper viscose requires a smaller quantity of the coagulating agent for immediate coagulation ; thus the number of cubic centimetres of coagulating agent required is the less the greater the degree of ripeness of the viscose. This number can therefore be used as a direct measure of the degree of ripeness.

The figure which is obtained depends on various factors, more particularly on the nature of the coagulating agent which is chosen, on the concentration of its solution, the degree of dilution of the viscose and the temperature. Therefore, numbers can only be compared which have been obtained by precisely the same method. All possible coagulating agents may be used, such as acetic acid, alcohol, ammonium sulphate, zinc sulphate, ammonium chloride, and others. Ammonium chloride has been found to be one of the best. Hottenroth (*loc. cit.*) dilutes 20 gm. of viscose with 30 c.c. of distilled water, and titrates with 10 per cent ammonium chloride solution, with stirring, until coagulation occurs. The temperature of the solution should be exactly the same for all determinations. The following figures, obtained by him, with 5 per cent acetic acid and 10 per cent ammonium chloride solution, will show the course of the reaction with a definite spinning viscose—

	Ammonium chloride c.c.	Acetic acid c.c.
1. Slightly ripened . .	13·1	26·5
2. ,, ,, . .	12·5	24·2
3. Almost ripe . . .	11·2	22·8
4. ,, ,, . . .	10·1	19·5
5. ,, ,, . . .	9·6	18·2
6. ,, ,, (Optimum) .	8·2	14·0
7. Ripe	7·8	11·5
8. ,, ...	6·7	10·7
9. Over-ripe . . .	5·2	8·5
10. ,, . . .	4·7	6·5
11. ,, . . .	3·8	6 1
12. Coagulated . . .	—	—

If, therefore, the ammonium chloride figure, for example, has been empirically determined, at which the normal viscose of

a works yields the best results on spinning, it is easy by this method to determine the optimum degree of ripeness of any such viscose.

Attempts have also been made to utilize the decrease of combined xanthate alkali during ripening (see page 286) which may be determined by the iodine reaction described on page 279, in order to determine the degree of ripeness. Hottenroth repeated the reaction described by Cross and Bevan, and communicated the following results of his experiments (*Chem. Ztg.*, 1915, page 119)—

"If one uses 2·5 gm. of viscose for analysis, then if this contains 6 per cent of cellulose, 9·2 mgm. of alkali correspond to the C_{24} formula. On testing a viscose sample at all stages of ripeness I obtained, for example, on 11 consecutive days the following values for the contents of xanthate alkali in 2·5 gm. of viscose. (The descriptions of the various degrees of ripeness correspond to a test which was formerly much used by viscose silk manufacturers but which, as already mentioned, only gives rough approximate values)—

1. Unripe	17·68 mgm.	7. Ripe	6·20 mgm.
2. Still unripe	13·92 „	8. Ripe	5·90 „
3. Very weakly ripe	10·96 „	9. Over-ripe	5·00 „
4. Weakly ripe	9·76 „	10. Over-ripe	3·60 „
5. Weakly ripe	7·80 „	11. Coagulated	0·08 „
6. Almost ripe	6·69 „		

It is, however, by no means easy to carry out this determination, and useful results are only obtained if very careful precautions are taken; more particularly, the determination must be carried out extremely rapidly, although at least two minutes must be allowed to lapse between the addition of the acid and the determination. Naturally, in such a difficult analysis the most exact uniformity of operation is necessary. It would be quite impossible to use the method for rapid determinations in a works which requires a large number of analyses daily."

In works, the ripening of the viscose is usually carried out in a special chamber maintained at an exact temperature, and known as the "ripening chamber." Ripening can be carried out either in stationary containers or in large revolving pans

mounted on trucks, which are conveyed on rails from the filter room to the ripening room. The ripening containers are provided with a water jacket, so that by cooling or warming ripening can be carried out at any desired temperature, and can thus be retarded or accelerated. It has already been mentioned that the ripening process takes place more rapidly at higher temperatures. The ripening can safely be carried out, for example, at temperatures of 70° to 80° C., in order to promote rapid ripening of the viscose, according to British patent 17,502/1902, German patent 183,623, and Austrian patent 323,473 of the Ver. Kunstseidefabriken A.-G., Frankfurt. In some patent specifications, even warming to 90° C. is recommended ; thus, for example, in German patent 223,736 of the Soc. de la Viscose, and British patent 8179/1907, and Austrian patent 323,473 of the Ver. Kunstseidefabriken A.-G. Moreover, these patents deal with a process which must also be described here, according to which the viscose is simultaneously ripened and concentrated until it contains 12 to 15 per cent of cellulose. This concentration is achieved in an evacuated space at as low a temperature as possible, by heating. After a sufficiently high concentration has been attained distillation is stopped, and the ripening process is, if necessary, completed.

We have already mentioned that alkalis retard the ripening process, or if added later may even reverse it, and that on the other hand the addition of a salt accelerates the process (page 280). The latter phenomenon is utilized by Soc. Soie de Chardonnet, Besançon, according to British patent 1436/1911, German patent 270,051, Swiss patent 54,834, and French patent 430,445, in order to dispense with the usual ripening process, by increasing the coagulation velocity to such an extent, by the addition of neutral salts to the viscose, that the latter may be spun at once. The actual process is easily understood in the light of the above theoretical explanations of the ripening process, but the process has not been introduced in practice on account of the unnecessary and expensive complication which it introduces. Similarly, according to the process of the German Zellstoff-Textilwerke, Elberfeld (German patents 339,050 and 342,641), considerable quantities of a

neutral salt are added to the viscose solution, or even to the alkali-cellulose, a process which is analogous in principle to that described by the Soc. Soie de St. Chamond, in British patent 24,291/1914, Swiss patent 71,312, and French patent 474,777, according to which the free caustic soda of viscose and a portion of the soda combined with the cellulose are neutralized by the addition of alkali bicarbonate or bisulphite or acid alkali phosphate ; for example, per 100 kg. of cellulose, 10 to 15 kg. of sodium bisulphite or 8 to 12 kg. of sodium bicarbonate or 13 to 20 kg. of di-sodium phosphate are to be used. It is stated that viscose solution treated in this way requires less precipitant than the usual alkaline solution. In German patent 312,392, Linkmeyer and Hoyermann propose the addition of substances containing amino- or imino-groups to viscose. By this means, the stability of viscose solutions is said to be increased to such an extent that satisfactory thread formation can be obtained even after weeks. Moreover, it is stated that the threads are distinguished by great strength, and that they are but slightly sensitive to water, particularly when a spinning bath is used containing formaldehyde. Even if this advantage is actually obtained, it is very questionable if it would compensate for the increased cost of materials and operation. In German patent 360,946, M. Luft proposes to add naphthenic acids or their salts to viscose, either during its manufacture or to the finished viscose solution. According to German patent 337,984, of Chemische Fabrik von Heyden A.-G., viscose solutions are spun after the addition of ammonia, or after a portion of the alkali has been replaced by ammonia ; whilst a process is described by Courtaulds, Ltd., in German patent 381,020, according to which a viscose is used obtained from cotton, to which very small quantities have been added of oleates, resinates or other compounds which reduce its surface tension relatively to the spinning bath.

J. A. Burette attempts to eliminate the ripening process by an entirely different method, which is described in French patent 430,221, already referred to. In our theoretical considerations on the ripening process we have already seen that during ripening the xanthic acid complex is gradually eliminated,

so that finally there are four cellulose residues to each xanthic residue. According to Burette, it is possible to obtain this compound, containing relatively little sulphur, in a single operation, by pressing the alkali-cellulose until its weight is 2·5 times that of the cellulose which is present, and then acting on it with 15 to 20 per cent of carbon disulphide only, in the following manner: the alkali-cellulose, which is broken up into flakes, is subjected to the action of carbon disulphide in the form of vapour whilst in thin layers contained, for example, in cages of perforated metallic sheet. The fact that the final product of the ripening process is so obtained does not appear to have been confirmed so far by others ; but apart from this question the process would probably be too sensitive and troublesome for works practice ; at any rate, it has not been practically applied anywhere.

Additions to viscose for the purpose of favourably influencing the formation of the fibre, of increasing its flexibility, and so forth, have often been proposed and used. We may refer, for example, to the addition of ethylene-thiohydrin or its esters, which is proposed by Höchster Farbwerke in German patent 368,045, additional to German patent 366,115.

Subsequent Treatment of Viscose. From the ripening tanks the viscose is conveyed to the spinning tanks, which are large cylindrical iron containers, usually vertical, from which it is then conveyed directly to the spinning machines. It is advisable to leave the viscose in the spinning tanks under vacuum for some time in order that even the smallest air bubbles may be carefully removed.

A special process for removing carbon disulphide, air and other gases from viscose, as completely as possible, was patented by the Soc. de la Viscose in British patent 5286/1904, German patent 163,661, Austrian patent 19,041, Swiss patent 30,768, U.S. patent 767,421, and French patent 340,690. The process consists in allowing the viscose to flow, under the action of a vacuum, in a thin layer over a cone which revolves inside a container, which may also conveniently have a conical form, and subjecting the material simultaneously to the kneading action of flat blades.

THE SPINNING PROCESS

The spinning of viscose, which is the next operation, is carried out essentially by the same method as that of other artificial silks. The necessary apparatus, more particularly the spinning machine, has already been described in detail in an earlier chapter, page 83 *et seq.* We may, therefore, immediately consider the spinning baths which are especially applied to viscose silk.

Viscose Spinning Baths. In a previous section we have already discussed the general qualities required of a spinning bath. What was there said is true for viscose spinning baths in particular, for there are a whole number of precipitants for viscose which are not suitable as a spinning bath, because they decompose cellulose xanthate too rapidly, with formation of an easily disintegrated, more or less irregular mass. Spinning baths for viscose may be divided into those which decompose xanthate and those which merely coagulate it. When considering the properties of viscose we already discussed the reagents which decompose and those which merely coagulate that substance (page 278 *et seq.*) to which we may refer in order to avoid repetition.

For spinning viscose silk, the most important reagents are salt solutions, dilute acids and mixtures of these.

Thus, the first viscose spinning bath patent of Chas. Henry Stearn (British patent 1020/1898, German patent 108,511/1898, Swiss patent 19,135, and U.S. patent 622,087) claims a solution of an ammonium salt, preferably ammonium chloride. In his later British patent 7023/1903, U.S. patent 716,778, and French patent 330,753, the same inventor states that a solution of ammonium sulphate is the best precipitant. In actual fact ammonium sulphate is a very useful precipitant, and is more particularly suited for the production of thick threads, such as artificial horse-hair. The first acid baths are also due to Stearn. In his British patent 2529/1902, and U.S. patent 725,016, he proposes as a precipitation bath for viscose, which has been purified by re-precipitation, dilute acids of various concentrations, these being sulphuric acid of about 9 per cent, hydrochloric acid of 7 per cent and acetic acid of 10 to 20 per cent concentration. He states that spinning should be carried out at 10° to 20° C., and that the acid neutralized by the alkali of the viscose should continually be replaced by further acid. According to this process, the acids may also be replaced by compounds which readily dissociate, such as aluminium or chromium sulphate.

The stickiness of the swollen thread which readily occurs when spinning viscose in baths containing ammonium salts and also in the acid bisulphate baths which will later be described, and which may lead to adhesion of the threads to one another on the spool, is reduced by the process originally proposed by Prince Guido Henckel von Donnersmarck, in British patent 16,604/1903, German patent 152,743, Austrian patent 16,112, and French patent 334,515, and German patent of addition 153,817 ; the process consists in the precipitation of finely-divided sulphides of heavy metals, such as FeS or As_2S_3 on to the fibre. This is effected by passing the threads, after their removal from the bath of ammonium salt, and before fixing and winding them, through a solution of the salt of the respective heavy metal, or by the addition of such a salt to the spinning bath.

A number of processes of spinning viscose silk are described by C. A. Ernst in his U.S. patents 792,888, 798,027, 863,793 and 896,715. In the first patent he proposes as a precipitant a saturated solution of sodium acetate in methyl-alcohol, to which 6 per cent of acetic acid has been added. The wound threads are to be fixed by subsequent treatment with a mixture of methyl-alcohol and acetic acid. Even though it were possible to obtain satisfactory results in this manner, the process would certainly be far too expensive. According to the second process, the precipitating liquid consists of a solution of sodium and ammonium bicarbonates together with ammonium sulphate, and the conversion of the threads into cellulose is to be effected by subsequent treatment with ammonium sulphate. In the last two patents, Ernst attempts to utilize the fact, which has already been referred to, that the addition of salts accelerates the decomposition of viscose, in order to avoid the special ripening process. He adds sodium sulphite to the viscose, or neutralizes a portion of the alkali of the viscose with acid or with an acid salt ; he then precipitates with sodium bisulphite solution or with a weak acid bath, followed by a subsequent treatment with sodium bisulphite.

The use of salts of organic bases, for example, of aniline, naphthylamine, pyridine and so forth, which is proposed by

Pissarev in British patent 16,583/1905, Austrian patent 29,835, and French patent 357,056, is impossible in practice on account of the relatively high price of those compounds.

On the other hand, the bath which is proposed by the Elberfelder Glanzstoffabriken in British patents 21,405/1907 and 5595/1908, German patent 240,846, French patent 394,586, Swiss patent 43,016, and U.S. patent 970,589, is of technical importance. It is assumed that the oxidation of hydrogen sulphide is suppressed by the addition of organic reducing compounds, such as glucose, glycerine and other polyvalent alcohols, fatty acids, and so forth, and that the separation of sulphur produced during such oxidation is thus avoided. As, moreover, these compounds coagulate but do not decompose viscose, the salt contents of the bath may be reduced accordingly. The following examples are given of suitable baths—

1. 10 sulphuric acid, 30 glucose, 60 water.
2. 9 hydrochloric acid, 10 glycerine, 81 water.
3. 8 sulphuric acid, 17·5 ammonium sulphate, 7·5 glucose, 67 water.
4. 8 sulphuric acid, 6 magnesium sulphate, 7·5 glucose, 78·5 water.

A very similar precipitating bath is proposed in French patent 400,577 of Soc. Pinel Frères ; namely, 30 glucose, 15 sulphuric acid (60° Bé.) and 55 water ; which, however, can be varied within wide limits according to the patent. According to British patent 406/1911, German patent 260,479/1911, Austrian patent 63,722, Swiss patent 57,506, French patent 434,501, and U.S. patent 1,045,731 of the Vereinigten Glanzstoffabriken, Elberfeld, a favourable action is exerted by a small quantity of a zinc salt or of a zinc compound, or of zinc itself to the acid bath, which forms a zinc salt with the latter. The following baths are given as examples—

1. 8·5 sulphuric acid, 9 glucose, 4 ammonium sulphate, 12 sodium sulphate, 1 zinc sulphate, 65·5 water.
2. 8 sulphuric acid, 10 glucose, 12 sodium sulphate, 1 zinc sulphate, 69 water.

The quantity of zinc salt is not to exceed 5 per cent of the weight of the bath.

These additions, more particularly that of glucose, have been found very satisfactory, as they favourably influence the production and properties of the thread. They are therefore still

much used, for example, in the form of molasses and so forth. In British patent 2992/1913, German patent 274,550 and patent of addition 283,286, Austrian patent 61,811, Swiss patent 62,315, U.S. patent 1,102,237, Belgian patent 253,454 and French patent 454,011, the Vereinigten Glanzstoffabriken propose the use of lactic, glycollic, citric and tartaric acids, which presumably have a similar action to glucose, but some of which are probably too dear to be applied for this purpose. (See also German patent 346,832 on the addition of lignoproteins to viscose.)

According to C. N. Waite's U.S. patent 816,404, a spinning bath is used consisting of a saturated sodium bisulphite solution containing 11 to 12·5 per cent of active sulphur dioxide, to which 10 per cent of a saturated solution of ammonium sulphate or sodium chloride is added. It is stated that under these conditions the sulphur of the viscose is converted into thiosulphate.

The cheapest, and at the same time the simplest possible spinning bath for viscose, is proposed by Max Müller in British patent 10,094/1906, German patent 187,947/1905, Austrian patent 33,678, French patent 365,776, Swiss patent 42,306, and U.S. patent 836,452, and consists of sulphuric acid in which a salt, preferably a sulphate, is dissolved ; for example, a very suitable spinning bath is stated to be a solution of 40 kg. of sodium bisulphate in 60 kg. of water, to which 7 kg. of 66 per cent sulphuric acid have been added. This bath contains 15 per cent of semi-combined and 4·3 per cent of free sulphuric acid, that is, a total of 19·3 per cent of titratable acid. V. Hottenroth found, however, that better results are obtained if free acid is avoided, that is, if one operates essentially with half-combined sulphuric acid and even adds neutral sulphate in addition. (See the patents relating to this subject, of Vereinigten Glanzstoffabriken ; German patent 287,955/1912, and Austrian patent 63,635.) E. Bronnert recommends a spinning bath which contains sulphuric acid and at least one of the salts occurring in the Stassfurt "Abraum" salts (British patent 170,313, Swiss patent 94,416, and French patent 515,332).

Later Viscose Spinning Patents. Long before the commencement of the Great War, viscose silk was spun with the above mentioned reagents, which have remained essentially the same both during and since the war until the present day ; they have merely been varied hundreds of times in detail in order to obtain new results of more or less importance. Many variations were, however, possible and their number naturally increased to an extraordinary extent, as the number of variable factors is very great in this case. Two problems were followed with special interest, and of the hundreds of viscose spinning patents by far the greater number attempted the solution of these ; they are, the production of as fine a quality of thread as possible and the spinning of the unripened viscose in order to reduce the ripening period, although there were a few patents which attempted the use of an over-ripened viscose for other reasons It is not possible to describe all these processes within the limits of this book, and we must, therefore, content ourselves with mentioning the most important results and referring the interested reader to the literature, and more particularly to the patents.

E. Bronnert worked on this question in great detail in the Research Institute of the Vereinigten Glanzstoffabriken and acquired a large number of patents, which contain a very large amount of information, although some of them deal with more or less known methods. (See British patents 163,466, 163,817, 166,931, 169,190, 170,024, 170,029, 170,322, 170,874, 171,125, 172,038, 174,960, 174,961 ; Swiss patents 87,535, 87,536, 87,736, 91,827, 94,412 to 94,421, 95,355 : French patents 510,803, 511,823, 512,248, 512,318, 514,774, 515,260, 515,491, 515,858, 516,091, 542,032 ; and Austrian patents 88,649, 88,651, and 88,652.) In the spinning solution he varied the degree of ripeness, the viscosity and the additions ; in the spinning bath he varied the composition, the concentration, the temperature, the degree of acidity and the various additions ; when spinning he varied the rate of flow of the viscose, the rate of withdrawal, the width of the spinning apertures, and the method of withdrawing the thread. He attempted to establish rules relating to the dependence of these various

factors on one another, and in many cases established mathematical formulae regarding these relations. He applied to viscose the stretch-spinning process, which had already been used for cuprammonium silk, and attained very fine qualities under definite conditions in this case also, namely, 1 to 6 deniers for the individual fibre. According to his statements, the concentration of acid should be the higher, the finer the thread which is to be produced. This statement is also said to be true when using highly-concentrated bisulphite solutions for obtaining very fine threads ; he mentions aldehyde-phenol-condensation products as additions to such bisulphite baths, stating that these may also be added to the viscose itself. It is stated that the addition of sulphurous acid or of a neutral or acid sulphite to the spinning bath or to the viscose prevents individual fibres from adhering one to another.

The above-mentioned relationship between the concentration of the bath and the fineness of the thread is said only to apply for a given nozzle aperture of 0·1 mm. For other nozzle apertures the concentration of acid to be used is stated to be related to that used for a normal nozzle aperture in the proportion of the cross-sections of the two apertures. It is stated that the nozzle apertures should be varied according to the viscosity of the spinning solutions, which would be a somewhat complicated procedure in works practice. He states that the normal spinning aperture of 0·1 mm. can be used satisfactorily for fine threads of 2 to 6 deniers if the supply of viscose is regulated to correspond with the quality of thread to be spun, taking into account the number of individual threads and the rate of withdrawal. Moreover, he states that for fine counts the ratio of the acid concentration to that used for coarser counts should be approximately inversely as the ratio of the square roots of the thickness of the two threads. When using a bath containing ammonium sulphate and sulphuric acid for threads of less than 6 deniers, the sum of the weight of the free sulphuric acid and of half the weight of ammonium sulphate should, he says, be inversely proportional to the approximate values of the square roots of the thicknesses of the threads. When using a spinning bath which contains both free sulphuric

acid and an aromatic acid, such as benzene sulphonic acid, the strength and elasticity of the threads are said to depend entirely on the degree of ripeness of the viscose, unripe viscose giving a weaker but extraordinarily elastic thread, whilst ripe viscose gives a strong but less elastic thread. Also the effect of the degree of ripeness of the viscose when using a sulphuric acid bath is said to be much diminished when an oxycarboxylic acid, such as lactic acid, is added to the bath. The well-known addition of glucose, or other polyvalent alcohols, is also recommended for the fine spinning process. It is stated that a solution containing 0·5 to 1 per cent of benzene sulphonic acid together with lactic acid, sugar and ammonium sulphate, forms an excellent bath for the stretch-spinning process.

Similar variations of the above-mentioned factors are contained in the following patents: German patents 351,871, 353,483, 369,175, and 417,092 of Chemische Fabrik v. Heyden A.-G.; German patents 308,427, 357,668, and 411,600, and French patent 510,576 of Vereinigten Glanzstoffabriken; German patent 358,145 of Linkmeyer; Swiss patents 84,599 and 85,532, and French patents 518,410 and 518,451 of Glanzfäden A.-G.; Swiss patents 86,010 and 87,368, and Austrian patent 89,148 of B. Borzykowski; British patent 171,776, Swiss patent 94,422, and French patent 522,802 of Technochemia A.-G., Glarus; German patent 324,433 of J. C. Hartogs; French patent 498,536 of T. H. Verhave; French patent 541,821 of Kämpf; British patents 162,759 and 167,076 and French patent 557,158 of Bouillon and Worms; German patent 338,360 of L. Leduc and others.

According to German patent 356,309, of Zellstoffabrik Waldhof and V. Hottenroth, a spinning bath can be directly prepared which contains acid, salt and glucose, by hydrolysing cellulosic material with acid, for example sulphuric acid, and partially neutralizing the filtered acid sugar solution so obtained. According to German patent 391,159, O. Kohorn & Co. and A. Perl obtain in a similar manner an acid bath containing d-mannose.

An interesting alkaline spinning-bath for viscose is that described by Courtaulds, Ltd., in German patent 411,167, which consists of a solution of sodium silicate in the form of $2Na_2O + 7SiO_2$, for example in a 20 per cent solution. The precipitated fibre, which is presumably still soluble in water, is then fixed with sulphuric acid or the like. Water-soluble threads which are subsequently fixed are also obtained according to the above-mentioned German patents 351,871 and 369,175 of Chemische Fabrik von Heyden A.-G. In order to render harmless the hydrogen sulphide which is produced during the spinning process, and which interferes with the regular production of the thread, Glanzfäden A.-G. proposes in German patent 388,917 to add to spinning baths of acid character oxidizing agents which are not decomposed by the acid, such as per-acids and per-salts, or to produce these within the bath

by electrolysis. In German patent 385,769, Dr. M. Müller claimed spinning baths consisting of acidified solutions of lignin-sulphonic acid, obtained from sulphite pulp liquor. The same inventor, jointly with H. Voss, proposes in German patent 359,768 to obtain spinning baths of sodium bisulphite by passing sulphur dioxide into the press liquors from the manufacture of alkali-cellulose.

AFTER-TREATMENT OF VISCOSE SILK

With regard to the general processes of after-treatment, such as washing, drying, rewinding, doubling, reeling, bleaching, soaping and so forth, the statements in the earlier sections apply.

We may refer here to a mistake which is frequently made. If the spools or cakes in the spinning-pots are allowed to stand for some hours before washing, for the purpose of more thorough fixation, great care must be taken that the threads remain perfectly moist and do not become dry locally, as the mass of thread is soaked in acid or acid salt solution which would destroy the thread during drying, in consequence of increased concentration.

With regard to steaming of the thread, see German patent 416,210.

Desulphurizing. A special after-treatment peculiar to viscose silk is desulphurizing, an operation which is in many respects analogous to the denitration of collodium threads. This operation is also carried out in hank form and alkali sulphides are used as the effective desulphurizing agents. The hanks are turned in an alkali sulphide bath in vats, as previously described. Usually, a bath is used containing about 1 per cent of sodium sulphide at a temperature of 40° to 50° C. The operation may be complete in 15 to 20 minutes, but according to the character of the goods the temperature and so forth, may last for $\frac{1}{2}$ to 1 hour.

As in the case of denitration, the process may be checked by titration with iodine solution. According to the equation, $Na_2S_3 + I_2 = 2NaI + 3S$, the polysulphide requires 254 gm. iodine per 142 gm. Na_2S_3. After it has been converted into sulphide, three times the quantity of iodine, namely 762 gm., is required according to the equation $3Na_2S + 3I_2 = 6NaI + 3S$.

In German patent 360,945, M. Luft states that he has found that the power of absorption of viscose silk for soaps, impregnating agents and so forth, is particularly good during the desulphurizing process, and he therefore treats the fibre with soaps, emulsions, or impregnating agents, and so forth, in presence of alkali during desulphurization. In German patent 279,310, Courtaulds, Ltd., describe a process of preventing sulphite solutions from forming polysulphides during the absorption of sulphur. Glucose is added to the warm alkali sulphide baths in the presence of substances of alkaline reaction, in the proportion in which free sulphur is present in the bath. The operation is controlled by titration with iodine solution. The process is said to be applicable both to the denitration of collodium silk and to the desulphurization of viscose silk.

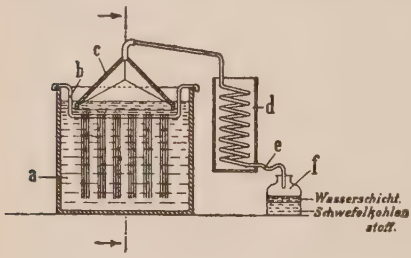


Fig. 87. Kämpf's Apparatus for Carbon Disulphide Recovery

Wasserschicht denotes "aqueous layer"
Schwefelkohlenstoff denotes "carbon disulphide"

The yellow colour of the hanks turns to greyish-green during desulphurization; before they are entered into the bleaching bath they are well washed in order completely to remove the remains of the desulphurizing bath from the thread.

Recovery of Sulphur. As will have been gathered from our description of the manufacture of viscose silk, the valuable chemicals which are used are caustic soda for the alkali-cellulose, and sulphur—which is more particularly used in the form of carbon disulphide for xanthation, but also in the form of other sulphur compounds during spinning. It is obvious that it is economically important to recover these materials.

The regeneration of the alkali has been already discussed on page 271 *et seq.*

The recovery of the sulphur has been attempted by many methods. According to German patent 359,685, A. Kämpf provides the washing containers *a*, in which the freshly spun viscose silk is entered on the rods *b*, with a hood *c* to which a condenser *d* is attached, as shown in Fig. 87. On treating the bobbins or hanks with warm water, carbon disulphide escapes from the container and is condensed by the arrangement *d*, *e*, *f*, and collected.

The carbon disulphide in the waste gases was formerly frequently absorbed by oils or was burnt to SO_2 in air. Both processes offer certain disadvantages. The former requires elaborate apparatus and the recovery is fairly complicated ; according to the latter, carbon disulphide is certainly removed, but the sulphur is not rationally recovered. According to German patent 412,113 of Herminghaus & Co., Hesse and Rathert, better results are obtained if the waste gases are treated with oxidizing agents such as hydrogen peroxide, chlorine liquor, and the like, in presence of alkali, in spray washers, absorption towers, and so forth. According to German patent 338,291, H. Voss fixes the viscose threads precipitated by sulphites in closed containers, collects the sulphur dioxide which is evolved, and recovers the separated sulphur by filtration. E. Schülke treats the spinning baths or waste gases containing the sulphur compounds with hydrochloric acid containing chlorine, which causes sulphur to be separated in a form which can be filtered. In German patents 368,969, 370,592, and 372,353, Herminghaus & Co., Hesse and Rathert describe a process for the utilization of waste liquors and other by-products of viscose manufacture, which consists mainly in coagulation by heating, separation of the insoluble products, and utilization of the filtrate, which contains alkali sulphides, for the absorption of CS_2 and H_2S. It is stated to be useful to treat the coagulated residues with small quantities of metallic oxides, peroxides, and so forth, in order to avoid any noxious odours.

CHAPTER XII

MANUFACTURE OF CELLULOSE ACETATE SILK

Cellulose acetate silk takes up a special position among artificial silks. According to its chemical nature it may be classed with collodium silk as a cellulose ester silk, as both the acetates and nitrates of cellulose are true esters ; but whilst in the case of collodium silk the ester groups are practically eliminated completely by denitration, with re-formation of cellulose in the form of hydrate, cellulose acetate silk offers the great advantage that no deacetylation is required, as it is not readily inflammable. Acetate silk remains, therefore, unchanged as a cellulose acetic acid ester (acetyl-cellulose or cellulose acetate) to which circumstance it owes its peculiar character ; for there is a peculiarity which may be noted in both organic and inorganic chemistry, that free hydroxyl groups cause ready absorption of water or even complete solubility in that liquid ; whereas when they are fixed by esterification, the compounds in question become less soluble or insoluble in water and absorb water less readily ; that is, they become faster to water, and less capable of gelatinization.

Cellulose Acetates. (Acetyl Celluloses)

Historical. The first cellulose acetate was prepared by Schützenberger in 1865, by heating cellulose with acetic anhydride in a closed tube ; (Schützenberger and Naudin, *Zts. f. Chem.*, 1869, page 264). Franchimont (*Ber.* 12, page 1941), who worked at the same problem after 1879, was the first to carry out this process of esterification under the influence of a catalyst, although he did so under otherwise unfavourable conditions, namely, at about 140° C., the boiling point of acetic anhydride. Later, Skraup (*Ber.* 32, page 2413) carried out experiments on the acetylation of cellulose under similar conditions ; in common with the two above-mentioned investigators, his work was carried out from a purely scientific

standpoint. The two last-mentioned experimentalists obtained considerably degraded products, for example, acetylated triglucose, and so forth. During the further continuation of his experiments, Franchimont isolated a compound which he called "the acetic ester of cellulose" (*Rec. Trav. Chim. des Pays Bas.*, 18, page 474). The properties noted by him make it clear, however, that he had obtained neither the normal triacetate nor a closely related transformation product of this latter.

The first process of acetylating cellulose suitable for technical requirements was due to Cross and Bevan, to whom were also granted the first cellulose acetate patents (see German patents 85,329 and 86,368. German patents 105,347 and 112,817 also refer to work by these investigators). They acted on regenerated cellulose with acetyl chloride, or acetyl chloride and acetic anhydride, in presence of zinc acetate or magnesium acetate, with or without the addition of inert solvents. These patents were acquired by Prince Guido Henckel von Donnersmarck, and cellulose acetate was first manufactured commercially at the Fürst Guido Donnersmarckschen Kunstseiden- und Acetatwerken at Sydowsaue, near Stettin, in 1898. The first cellulose acetate silk was also produced in the experimental plant erected at these works (which did not, however, produce any marketable product), after the use of cellulose acetate for this purpose had first been proposed by Mork, Little and Walker in 1902, in their American and British patents, which were also partially acquired by Prince Donnersmarck. (See British patent 20,672/1910 and U.S. patents 712,200, 792,149, and 1,107,222.)

Subsequently the problem of the acetylation of cellulose, which had thus been brought to public notice, and which appeared very promising, attracted a large number of workers, who more or less successfully developed this branch of manufacture further; more particularly, L. Lederer, A. Wohl, Miles, A. Dreyfus, A. Eichengrün, Farbenfabriken vorm. Friedrich Bayer & Co., Knoll & Co., Chemische Fabrik von Heyden, A.-G. für Anilinfabrikation, Badische Anilin-& Soda-fabrik, and others. We will return to the consideration of the patents due

to these workers when considering the various processes in detail.

Theoretical Considerations. The acetylation of cellulose is completely analogous to its nitration (see page 168 *et seq.*), being also an ordinary esterification process. One difference is that acetylation does not take place so easily. In contrast to nitric acid, even highly-concentrated acetic acid only acts very slowly on cellulose, and acetic anhydride, which is also used for acetylation, only acts at high temperatures and high pressures, or considerably more readily in the presence of a catalyst, more particularly of a dehydrating agent, such as concentrated sulphuric acid, zinc chloride or similar substances. The reaction then takes place according to the equation—

$$2C_6H_{10}O_5 + 3(CH_3CO)_2O = 2C_6H_7O_5(CH_3CO)_3 + 3H_2O$$

The equation so frequently reproduced, for example, by Ost (*Zts. f. angew Chem.*, 1919, page 67), and by Heuser (*Lehrbuch der Cellulosechemie*, 2nd Edn., page 46), in which 3 molecules of acetic anhydride react with 1 molecule of cellulose with production of 3 molecules of acetic acid, does not correspond to the pure esterification but includes the reaction of the water which is liberated, with excess of acetic anhydride, and thus corresponds to the proportions actually required.

A very complete analogy is found between the acetylation and nitration processes, more particularly if sulphuric acid is used as a catalyst, as in that case (see page 168) a condition of equilibrium is attained, in which esterification and saponification balance, so that here also the highest stage of acetylation (the triacetate) is only obtained admixed with less acetylated products. In this case also, sulphuric acid esters or mixed cellulose esters (sulpho-acetates) occur as by-products. In the case of acetylation in presence of sulphuric acid, however, a relatively considerable degradation of the cellulose molecule (acetolysis) also occurs, which, under certain conditions, may lead to the production of cellulose-dextrines and even to sugar derivatives.

This acetolysis, which was first observed by Skraup, must not be confused with the ordinary hydrolysis of cellulose by

acids. Both finally lead to the same products, namely, sugars or sugar acetates ; but the intermediate products leading to these differ in the two cases. Moreover, the acetolytic degradation of cellulose occurs considerably more readily than hydrolysis ; whereas cellulose is only converted into sugar with difficulty by dilute acids, it is converted with relative ease into cellobiose octoacetate or dextrose pentacetate by mixtures of acetic anhydride and sulphuric acid.

As this acetolytic degradation of cellulose always occurs to an extent which is dependent on the temperature, quantity of acid and so forth, when acetylating in presence of sulphuric acid, the acetates obtained in this case are no longer derivatives of pure cellulose, but of more or less degraded products, hydrocelluloses, and so forth. The degree of degradation is dependent on the quantity of sulphuric acid, the duration of the reaction and the temperature of the reacting mixture.

Finally, as in the case of nitrates, it is not possible in the case of the acetates to produce lower acetylation products (mono- or diacetates) by direct means. If the calculated quantity of acetic anhydride required for such an acetate is used, a portion of the cellulose merely remains unattacked This is also the case when the sulphuric acid is replaced by other catalysts. So far, it has only been possible to obtain a less highly acetylated product (the diacetate) by saponification of the most highly acetylated product (the triacetate).

Leaving minor differences out of consideration, four main varieties of cellulose acetate can be distinguished—

1. The triacetate, soluble in chloroform and insoluble in acetone, which is usually obtained by normal acetylation correctly carried out, and which forms an intermediate stage in the production of the important class of acetone-soluble products referred to under 3.

2. Acetates containing much sulphoacetate, soluble in alcohol and sometimes soluble in water, which are obtained by esterification in presence of little acetic anhydride and much sulphuric acid. (See, for example, German patents 153,350 and 185,837 of Farbenfabriken vorm. Friedrich Bayer & Co.)

3. The " unbroken " acetates, soluble in acetone, which are

the most valuable representatives of these compounds, and which are obtained from the triacetates referred to under 1.

4. The technically worthless acetates, which are also soluble in acetone, but are highly degraded, the solubility in acetone of which is essentially due to a very large degree of acetolysis.

We are only interested here in the acetates of classes 1 and 3 ; that is, those soluble in chloroform, and more particularly those soluble in acetone which were called by Knoevenagel the " unbroken " acetates, which are alone of general technical value and more particularly of value for the artificial silk industry. The principal materials, both for general purposes and for the production of acetate silk, are constituted by the acetone-soluble acetates of class 3. We have already mentioned that these acetone-soluble acetates are not obtained directly, as a primary acetylation product, but that they are obtained from the chloroform-soluble triacetates of class 1 as an intermediate stage.

The conversion of the chloroform-soluble product, which is insoluble in acetone, into the acetone-soluble product, is carried out by the action of water, preferably in the presence of a mineral acid, on the original acetate, dissolved, for example, in glacial acetate acid. In spite of detailed investigation by Knoevenagel, Ost and others, the mechanism of this process has not yet been fully explained, and very varying views on its nature are still held. Ost considers the solubility in acetone to be a consequence of hydrolysis and simultaneous saponification, that is, conversion of the triacetate into the diacetate. We are unable to agree with this view, or at any rate to consider it as proved. It does not agree with the fact that acetates completely soluble in acetone can be obtained from the triacetate, as Ost himself has shown, the acetyl contents of which are still very nearly identical with those of the triacetate, and far removed from those corresponding to a diacetate. (See also, Knoevenagel, *Zts. f. angew. Chem.*, 1914, pages 57 and 508.) It thus appears that saponification is not essential for the conversion into an acetate soluble in acetone. Similar considerations apply to the hydrolysis or hydration. This is, perhaps, merely a by-reaction, which possibly merely

initiates the conversion and promotes or accelerates it. Moreover, it is very possible that the hydrolysis which usually occurs during the manufacture of the acetate soluble in acetone, and the more or less considerable liberation of acetic acid (saponification), which has undoubtedly been proved, may be considered as reactions which are with difficulty avoided when using these acid-hydrolytic agents, that is, as secondary occurrences to which the solubility in acetone is in no way due; this, on the other hand, may be due to some molecular transformation, possibly to a depolymerization of the cellulose molecule initiated by the hydrolysis. This view is also taken by Knoevenagel (see *Zts. f. angew. Chem.*, 1914, page 508), and is expressed in German patent 297,504 of Knoll & Co., according to which the basis of the new process consists in the attainment of complete solubility in acetone, with avoidance of decomposition of the cellulose ester so far as possible. In any case, it appears to us quite inadmissible to consider the acetone-soluble acetates as diacetates, as is so frequently done. This view is not merely in contradiction with the facts already cited, but also with the fact that the products revert to a condition insoluble in acetone when the acetyl value is reduced to that of the diacetate, as is also shown by Ost's experiments.

MANUFACTURE OF THE CELLULOSE ACETATES

Cellulosic Raw Material. For the production of cellulose acetates the same raw material is used as for that of the nitrates; that is, more particularly cotton, in the form of linters, or spinnery waste, paper from well-disintegrated wood-pulp, regenerated cellulose—for example, artificial silk waste—and so forth. In contrast to cellulose nitrate, however, excellent acetates can be produced from strongly-hydrolysed cellulose or hydrocellulose. This is not surprising, as no cellulose acetates are derivatives of pure cellulose, as already explained, but of more or less considerably hydrolysed degradation products, the acetylation being always accompanied by acetolytic degradation of the cellulose, which may, however, occur to varying degrees according to the catalyst which is used and to the other conditions of operation. Mercerized

cellulose and oxy-cellulose have also been used as raw materials for the production of cellulose acetate. As shown by Ost and Westhoff (*Chem. Ztg.*, 1909, page 198), the former is acetylated much more slowly than non-mercerized cellulose. Both Franchimont (*Rec. trav. Chim.*, 1883, pages 241 to 245), and Vignon and Guérin (*Bull Soc. Chim.*, 1901, page 139) obtain cellulose acetate from oxy-cellulose. The products show much the same solubility conditions as the normal acetates, but reduce Fehling solution strongly. Cross and Bevan, according to whose process the first cellulose acetates were produced on a technical scale, used cellulose hydrate as their raw material, in the form of cellulose regenerated from viscose or from cuprammonium solutions. Lederer, who was the first to use sulphuric acid as a catalyst, first restricted his claims very surprisingly to the use of hydrocellulose, although non-hydrolysed cellulose can be used directly in presence of sulphuric acid, as was shown by Farbenfabriken vorm. Friedrich Bayer & Co. (German patents 159,524 and patent of addition 185,837, also German patent 163,316). It is only in his later patent, German patent 163,316/1901, that Lederer also uses cellulose, or carries out hydrolysis and acetylation in one operation, by warming cellulose with a little sulphuric acid in presence of glacial acetic acid to 60° to 70° C., and then adding acetic anhydride or acetyl chloride. When using hydrocellulose, however, the reaction takes place considerably more rapidly. It is found that so long as the raw material is a pure cellulose, its exact character has no influence on the effect of the acetylation; that is, when the process is properly carried out, the final product is always a cellulose triacetate soluble in chloroform.

To-day, pure cellulose in the form of cotton (linters and so forth), or of pure wood-pulp paper, is the usual material for the production of cellulose acetate.

The process described by the Badische Anilin- & Soda-fabrik in German patent 184,145, is to be noted, according to which cellulose or mercerized cellulose in a moist condition is acetylated with acetic anhydride and a catalyst such as sulphuric acid, organic sulphonic acids, or phosphoric acid.

With regard to the pre-treatment of the raw material for the purpose of purification, see page 61 *et seq.*

Acetylation. In the manufacture of cellulose acetates, esterification is now always carried out by means of acetic anhydride in presence of a catalyst. Acetyl-chloride, which was formerly used, for example, in the first process of Cross and Bevan (German patents 85,329 and 86,368), and by A. Wohl (German patent 139,669/1899), is no longer used for the purpose. Its use offers no advantages, and it is less easily manufactured and handled than acetic anhydride, and moreover, in its absence no hydrochloric acid is evolved during the reaction, which might exercise undesirable secondary effects on the cellulosic raw material.

The various processes differ merely in the conditions under which the acetic anhydride is used, and more particularly in the nature of the catalyst, of which a large number have been discovered in the course of time, and protected by patents.

Catalysts. The technically most important catalyst is sulphuric acid, which was first used by Lederer (German patents 118,538, 120,713, 163,316, and 200,916). It is the most rapid of all catalysts, but must be used with care ; as already mentioned, particularly at high temperatures, it gives rise to strong acetolytic degradation of the cellulose molecule, apart from the esterification. In order to avoid this degeneration as far as possible, acetylation in presence of sulphuric acid must be carried out at as low a temperature as possible, and the acetylating mixture must not be allowed to act on the cellulose for a longer period than is absolutely necessary. We have already referred to the simultaneous production of mixed esters (sulpho-acetates).

A whole series of sulphuric acid derivatives have been proposed as catalysts by various inventors, but have attained no practical importance. Phenol sulphonic acid and naphthol sulphonic acid, which were proposed by Mork, Little and Walker, in U.S. patent 709,922, appear to have acted merely in virtue of the adherent sulphuric acid, as according to other workers the pure sulphonic acids have absolutely no action. The sulpho-aliphatic acids proposed by Pauthonier, in British patent 27,101/1909 and French patent 409,465, must also presumably have owed their catalytic action mainly to the sulphuric acid which they

contained. It is probable that compounds which are capable of liberating sulphuric acid may have owed their catalytic activity to this compound only, for example, in the case of dimethyl sulphate (Chem. Fabrik Flora, British patent 9998/1905, U.S. patent 826,229, French patent 345,764); ether sulphuric acids and nitrosyl sulphate (lead chamber crystals), (H. Dreyfus, French patents 430,606 and 413,671); sulphuryl chloride, pyrosulphuryl chloride and chlorsulphonic acid (Farbenfabriken vorm Friedrich Bayer & Co., German patents 237,765 and 237,766; also Chem. Fabrik von Heyden, British patent 24,382/1910 and French patent 423,179). Further sulphuric acid derivatives which may be mentioned are: pyridine sulphate and its homologues, or quinoline sulphate (C. Claessen, German patent 222,450), also sulpho-acetic acid, used by the Société an. d'Explosifs (French patent 385,180), and sulphinic acids, patented by Knoll & Co., in British patent 2026/1907, German patents 180,666, and 180,667, Austrian patent 33,508 and French patent 369,123.

The use of phosphoric acid, instead of sulphuric acid, was proposed by Landsberg in French patent 316,500/1901, whilst Miles (U.S. patent 733,729/1903) recommends the anhydrides of mineral acids as catalysts.

Other acids, more particularly the monobasic, volatile mineral acids (hydrochloric, hydrobromic, hydriodic and nitric acids) are proposed by Knoll & Co., in British patent 2026B/1907, German patent 201,333, U.S. patent 891,218, and French patent 373,994, but have acquired no technical importance, and are not used. Sthamer (French patent 308,506/1901) had already discovered the catalytic action of hydrochloric acid gas during acetylation. The A.-G. für Anilinfabrikation propose the use of chloracetic acids and their homologues, in German patent 198,482, and French patent 368,728. The use of these is also proposed under somewhat different conditions by Knoll & Co., in German patent 203,642.

The catalyst second in technical importance to sulphuric acid is zinc chloride, first proposed by Knoll & Co. in British patent 2026A/1907, German patent 203,178, and Austrian patent 41,831), which is an excellent catalyst for the acetylation process, and has a considerably milder action than sulphuric acid. It exercises but a very slight acetolytic action on the cellulose molecule and the resaponification of the ester is so small that a condition of equilibrium is practically attained with the formation of triacetyl cellulose or triacetyl hydrocellulose, whilst when using sulphuric acid the pure triacetate is not fully attained, as shown by the acetyl contents of the acetates which are produced.

The neutral salts, other than alkali salts, claimed by Knoll & Co. in the same patents, have a considerably milder action than sulphuric acid and are usually considerably less active

than zinc chloride. The patent specification mentions the following salts as utilizable, apart from zinc chloride: Ferrous sulphate, ferric sulphate, ferric chloride, zinc sulphate, copper sulphate, stannous chloride, antimony trichloride and calcium chloride. The sulphates of hydrazine and hydroxylamine, the use of which is claimed by Scheering and Loose in British patent 27,228/1912, must also be mentioned here.

The Acetylation Process. Whether the acetate soluble in acetone is to be prepared, or the triacetate which is insoluble in acetone and soluble in chloroform, the latter product must first be produced, as it is always the intermediate product for the manufacture of the acetone-soluble acetate, as already explained. In the former case, however, it is not necessary to isolate the product soluble in chloroform, but it can be converted into the acetone-soluble product directly in the primary solution after acetylation has been completed.

Note. The term " primary acetate solution " denotes the first solution obtained on acetylation, which may, for example, contain excess of acetic anhydride, the glacial acetic acid used for diluting the mixture and as a solvent, and the catalyst, for example, sulphuric acid, together with the cellulose acetate product. If the acetate is precipitated from this primary solution, for example, with water, and is then washed, dried, and re-dissolved in a solvent such as chloroform, this is called the " secondary solution."

Production of the Triacetate Soluble in Chloroform. For esterification, 3 molecules of acetic anhydride are required to 2 molecules of cellulose (see equation, page 304) and 3 molecules of water are formed. In order that this water may not immediately prevent further reaction, it must be combined, conveniently with acetic anhydride, so that 3 molecules of acetic anhydride are required per molecule of cellulose, or 1·8 parts of weight of anhydride per unit weight of that substance. Even this quantity has been found too small in practice, and the best results are only obtained with a considerable excess of the anhydride. Ordinarily, about 4 parts of acetic anhydride are used to 1 part of cellulose.

Sulphuric acid is preferably used as the catalyst, as by its use the reaction is carried out most rapidly, as already stated, and it is also cheaper than most other catalysts.

Note. On mixing acetic acid, acetic anhydride and concentrated sulphuric acid in any sequence, a more or less vigorous evolution of gas is frequently observed. This always occurs if the glacial acetic acid contains formic acid. Hottenroth has shown (*Chem. Ztg.*, 1914, page 598) that this gas consists of carbon monoxide, which is produced by interaction between acetic anhydride and formic acid, according to the equation

$$CH_3CO \cdot O \cdot CO\,CH_3 + H \cdot COOH = 2CH_3 \cdot COOH + CO$$

As mentioned by Hottenroth, the reaction is very useful for the determination of very small amounts of formic acid.

Acetylation is carried out, for example, as follows: 1 to 1·5 kg. of sulphuric acid of 66° Bé. are added to 180 to 200 kg. of a mixture of equal parts of glacial acetic acid and acetic anhydride, with stirring; 25 kg. of air-dried cotton linters, containing 5 to 6 per cent of water, are then added, with constant mechanical stirring. By thorough cooling with water the temperature is maintained at about 20° to 25° C. The process may also be carried out by first introducing the cotton into the mixture of glacial acetic acid and acetic anhydride, and then adding the sulphuric acid gradually, with thorough stirring. The cotton swells rapidly, its fibrous structure disappears, and in the course of 5 to 6 hours—dependent mainly on the temperature—a syrupy primary solution is obtained, which is more or less clear according to the character of the raw material. The acetylation is not yet, however, finished, and the conclusion of the reaction can only be detected by removing samples of the syrup, which are poured into water.

As long as the acetyl-cellulose is thus precipitated in voluminous flocks, which dissolve in 60 to 80 per cent alcohol or in acetone on warming, intermediate stages of the esterification have alone been attained. The acetylation (that is, the formation of the triacetate) is only finished when the acetate is precipitated in a compact, tough, leather-like form: if the sample has been poured into water in a stream, the resultant precipitate usually consists of coherent worm-like threads which, after drying, are no longer soluble in the above-mentioned solvents, but easily dissolve in chloroform, after the addition of a little alcohol, if necessary. If this triacetate is to be isolated, the

contents of the whole batch are precipitated with water, either by pouring this into the primary acetate solution in large excess, or by pouring the latter into water. The precipitated acetate is then separated from the liquid on suction funnels or by centrifuging, washed with water until completely free from acid, and dried, for example, in vacuum drying chambers.

When zinc chloride is used as a catalyst, acetylation is carried out in an exactly similar manner, but takes considerably longer. The process may be carried out, for example, as follows: 15 kg. of powdered zinc chloride are dissolved in 80 kg. of glacial acetic acid, with warming; after cooling, 20 kg. of cotton are added, and 80 kg. of acetic anhydride are then gradually added, with cooling and thorough stirring or kneading. At temperatures below 20° C., acetylation in presence of zinc chloride requires 14 to 20 days, but can be considerably accelerated by warming; at 70° C. for example, it is complete in 8 to 10 hours. At this temperature, however, the acetylation is not easy to carry out, requires great practice and experience and easily gives rise to products of low value. It is better to carry out the operation by first adding the acetic anhydride at temperatures not above 20° C., and then raising the temperature to about 40° C., at which temperature the process is complete in about 2 days.

Precipitation of the acetyl-cellulose with water is certainly the simplest, cheapest and safest method, but has the disadvantage that both the excess of the relatively expensive acetic anhydride and also the glacial acetic acid used for dilution are only recovered as dilute, and therefore comparatively valueless, acetic acid. Other precipitants have, however, been proposed. Precipitation by hydrocarbons, such as benzene, naphtha, petroleum and so forth, was already described by Boesch in U.S. patent 708,457, and also in French patent 450,886 of the Soc. Debauge, and in French patent 15,894/1912 of Dreyfus. Carbon tetrachloride is proposed by Lederer in German patent 185,151/1905, and the same precipitant, together with substituted hydrocarbons in general, is mentioned in French patent 450,886 of Soc. Debauge, already referred to. Ethyl-ether was proposed as a precipitant by the

Fürst Guido Donnersmarckschen Kunstseiden- und Acetatwerken, in German patent 242,289/1910, and was actually used for a long period in the experimental works of that firm.

Any advantages hoped for by the use of these various precipitants were not realized on the anticipated scale, and they usually render the process considerably dearer. Water is therefore generally used for the isolation of cellulose acetate. The addition of water immediately stops both the acetylation and the hydrolysis or acetolysis, so that in this case special neutralization of the acetylation or catalytic reagents is unnecessary.

Such neutralization is proposed in various patents. Thus, according to Knoll & Co. (German patents 196,730, 201,910, 200,574) and Lederer (British patent 26,502/1906), basic salts are added to the solutions of the acetates before further treatment. According to German patent 260,984 of the Internationale Cellulosester-Gesellschaft, the primary solutions are first diluted with a non-solvent such as acetone, and then neutralized by the addition of salt forming bases.

It is an interesting fact that cotton may also be completely converted into the triacetate without destroying its original fibrous structure. This is attained, according to German patent 184,201/1904 of the Badische Anilin- & Soda-Fabrik, by carrying out the acetylation in presence of an indifferent non-solvent for acetyl cellulose, such as benzene. The same effect was achieved by Cross and Briggs in a somewhat different manner, according to German patent 224,330 and French patent 374,370, by using insufficient amounts of acetic anhydride and of a saline catalyst; and also by Monnet (German patent 258,879/1910) by the action of acetic anhydride in vapour form on cellulose which had been treated with acids.

Manufacture of the Acetone-soluble Acetate. The theory of the conversion of the chloroform-soluble acetate into the acetone-soluble product has already been referred to. The inventor of this process of transformation, and therefore the first to produce the acetone-soluble acetate, was Miles (British patent 19,330/1905, German patent 252,706—assigned to Farbenfabriken vorm. Friedrich Bayer & Co.—U.S. patent 838,340/1904, and French patent 358,079/1905).

Conversion Agents. For the conversion of the chloroform-soluble acetate into the acetone-soluble product, Miles used 10 per cent sulphuric acid, which was mixed with an equal volume of acetic acid in order to avoid local precipitation of

the acetate on pouring the dilute acid into the primary acetate solution. After it had once been shown, however, how valuable these acetone-soluble acetates were, a whole number of other conversion agents were claimed and patented by various parties.

The acetone-soluble cellulose acetates described by Walker (*Journal of the Franklin Institute*, 1907, page 136), which he obtained by acetylating in presence of benzene sulphonic acid as a catalyst, and by using definite proportions and temperatures, including large percentages of catalyst, must not be included in the valuable high molecular acetates. Such valuable acetates are, however, obtained by the process of Knoll & Co., who patented a long series of conversion agents. According to the main patent, German patent 297,507/1912, the conversion is achieved by warming the primary acetate with a little water and bisulphates or neutral sulphates of weak bases, such as methylamine sulphate. According to German patent of addition, 303,530, neutral solutions of nitrates or chlorides are used instead of the sulphates. According to German patent of addition 305,348, the charge is warmed with about 94 per cent acetic acid to 100° C., without a catalyst; and according to patent of addition 306,131, solubility in acetone is imparted, in the absence of water, by heating with glacial acetic acid and a small amount of an alcohol, such as glycerine, with or without a catalyst. A very similar process to the last but one, is that of the Verein für Chemische Industrie, Frankfurt a. M. (German patents 335,359 and 339,824, and French patent 455,117) according to which the primary acetate is heated to 100° to 110° C., with 95 per cent acetic acid. According to British patent 24,067/1906, and French patent 371,447 (with patent of addition 14,558), of Farbenfabriken vorm. Friedrich Bayer & Co., acetates soluble in acetone are obtained from the dry, primary acetate on standing with 10 per cent mineral acids. Scheering and Loose (British patent 27,227, French patent 452,347) convert the primary acetate into the acetone-soluble product by warming with aniline.

In the above-mentioned patent for the preparation of the acetone-soluble acetate, Miles gives the following directions: 100 parts of cellulose are treated for 8 hours at 60° to 70° C., with 240 parts of acetic anhydride, 400 parts of glacial acetic acid and 10 to 20 parts of concentrated sulphuric acid. The clear syrup is then " hydrated " by stirring into it 40 to 50 parts of a mixture of 100 parts of glacial acetic acid, 90 parts water, and 10 parts of concentrated sulphuric acid, after which it is allowed to stand for 12 hours at 50° C., and the acetone-soluble product is then precipitated by the addition of much water.

It is, however, advisable to carry out the acetylation at a

lower temperature, as described above for the manufacture of the chloroform-soluble triacetate.

Properties of the Cellulose Acetates. The chloroform-soluble cellulose triacetate is a light grey, hard, horny product. It is only slightly hygroscopic, and absorbs on the average not more than 0·5 to 3 per cent of moisture. It is soluble in chloroform (particularly easily after the addition of a little alcohol), formic acid (German patent 237,718), glacial acetic acid and particularly easily in acetylene tetrachloride (Lederer, German patent 175,379) ; and also in a mixture of acetylene tetrachloride and acetone (Lederer, German patent 240,751). Aniline and phenol are also stated to be excellent solvents. According to Ost (*loc. cit.*, page 87), 10 parts of hot phenol easily dissolve 1 part of acetate of any kind. The formic acid esters, the use of which was proposed by Wohl (German patent 246,651/1910) and by Mork (U.S. patent 972,464/1910), are also good solvents, but have acquired no technical importance. Formic acid itself also dissolves the various varieties of cellulose acetate readily, but has, of course, highly unpleasant properties as a solvent. It has, however, been proposed for the production of spinning solutions. Dichlorhydrin, epichlorhydrin, ethylene chlorhydrin, pyridine, beech tar creosote, methyl- and ethyl-benzoate, methyl-sulphocyanide in a mixture of alcohol and dichlorethylene (British patent 16,932/1910) and methyl-formate have also been described as solvents. It should be noted, however, that the solubilities in these reagents often vary considerably, according to the method of preparation of the material. These acetates are insoluble, or almost insoluble, in acetone, alcohols, ether, ethyl-acetate, benzene, benzine, dichlorethane, carbon tetrachloride, carbon disulphide, amyl-acetate and so forth. To the solutions in the above-mentioned solvents a definite amount of non-solvent can be added before precipitation of the acetate occurs.

A more or less considerable proportion of these acetates, "insoluble in acetone," is actually soluble in that reagent. This soluble portion shows, however, in no way the character of typical acetone-soluble acetate ; if, for example, it is separated by the evaporation of the filtered acetone solution,

it no longer dissolves completely in acetone, forms films of poor quality, and so forth. Ost (*Zts. angew. Chem.*, 1919, page 79), first pointed out this property and calls it "false" solubility. He has not, however, succeded in explaining the cause of these remarkable effects.

The behaviour of the primary triacetates with ethyl-acetate is very similar to that with acetone; but the proportions soluble in ethyl-acetate are usually somewhat smaller in amount.

There are also certain mixtures of liquids which individually are unable to dissolve cellulose acetate, but which when mixed form good solvents. An example is the mixture of dichlor-ethylene and alcohol, described in British patent 16,932/1910, French patent 418,309, and U.S. patent 988,965 of Farben-fabriken vorm. Friedrich Bayer & Co., which dissolves acetone-soluble acetates at the ordinary temperature, and the chloro-form-soluble variety on warming; also the mixture of alcohol with other non-solvents, more especially with benzene hydro-carbons, described by Eichengrün (German patent 254,385) which readily dissolves acetone-soluble acetates, particularly on warming.

Cellulose acetate may safely be warmed to about 150° C., and therefore temperatures of 110° to 120° C. can be used for drying. It holds water fairly tenaciously. In order to obtain small quantities rapidly in an anhydrous condition, it is therefore advisable to dry the acetate, in as finely-powdered a condition as possible, in a vacuum over sulphuric acid. Acetate insoluble in acetone shows no sharp melting point, as decomposition occurs between 200° and 250° C., before the melting point is attained.

Solutions of the acetate, for example, in chloroform, rotate the plane of polarized light to the left. By hydrolytic dissocia-tion the specific rotary power is gradually reduced, and finally changes to rotation to the right when hydrolysis is complete.

The dielectric constant of acetyl-cellulose is exceptionally high. A. Campbell (*Proc. Royal Soc.*, 1906, p. 196), found a value of 4·7 for air-dried acetate and of 3·9 for dry acetate, compared with air as unity. The insulating action of cellulose acetate is greater than that of rubber and of gutta-percha,

which is of great advantage when using acetate silk for insulating purposes.

The cellulose acetates are comparatively very resistant to water and dilute acids, and even to dilute alkalis, at the ordinary temperature. At higher temperatures both acids and alkalis have a saponifying action, as has also superheated steam. They are saponified in the cold by alcoholic alkali or alkali alcoholate. As Ost has shown, during alkaline saponification the cellulose complex is also attacked with formation of formic acid, acetic acid, and so forth; this method of saponification is, therefore, not suitable for the determination of acetyl-cellulose or of its contents of acetic acid. Dilute hydrochloric acid also saponifies gradually on heating. Strong sulphuric acid of 50 per cent strength, for example, dissolves the acetate and gradually saponifies it. It is also soluble in concentrated nitric acid, but according to Marsden (*Journal Soc. Dyers and Colourists*, 1905, page 107), is reprecipitated unchanged from the solution.

Fehling solution is usually reduced but little, or not at all, by acetyl-cellulose, probably for the reason that saponification must first occur.

The acetone-soluble acetates are usually light, snow-white, flocculent or granular powders, which differ mainly from the acetone-insoluble acetates by their solubility relations, but otherwise show similar behaviour. Apart from their solubility in acetone, they are also particularly soluble in methyl-ethyl-ketone, dichlorhydrin, epichlorhydrin, nitromethane (German patent 201,907), methyl-sulphocyanide, pyridine and so forth.

THE SPINNING OF ACETATE SILK

It will be seen from the above description that both high-boiling and low-boiling solvents are available for the production of cellulose acetate solutions. On glancing through the patent literature one finds, in fact, that most of these solvents have been tried or proposed by various parties for use in spinning solutions. Moreover, the number of non-solvents which can be used as spinning baths by the wet spinning process is very

large. By using relatively volatile solvents the dry spinning process can be used, as in the case of collodium silk, and in this case also, this is probably the method chiefly used.

It is, moreover, not necessary to separate the cellulose acetate after acetylation and to re-dissolve it, but the primary solution can be used directly as a spinning solution after suitable adjustment and, if necessary, neutralization of the catalyst, dilution with a volatile solvent, and so forth. The few works which at present manufacture acetate silk maintain their methods of manufacture as secret as possible. It is, however, quite clear that the spinning of the primary solution will be preferred, as this is simpler and cheaper. Moreover, in present manufacture, the valuable acetone-soluble acetate is always used for the production of artificial silk, and not the chloroform-soluble variety.

Lederer (British patent 7341/1903, French patent 330,714) dissolves the acetate, for example, in acetic acid, phenol, chloroform, and so forth, or in a mixture of various solvents, and spins in alcohol, benzene, ligroin or other liquids which mix with the solvents without dissolving the acetate. Mork, Little and Walker (U.S. patent 712,200), add to the spinning solution, if desirable, materials which render it flexible and elastic, such as oleic acid, acetylated castor oil, thymol, phenol and so forth. According to U.S. patent 792,149, they dissolve the acetate in 10 times its weight of chloroform, with the addition of cresol and oleic acid, and spin in paraffin hydrocarbons, petroleum naphtha, terpenes, turpentine, oil of camphor and so forth. Acetylene tetrachloride is used both by Lederer (British patent 6751/1905, German patents 175,379 and 188,542), and by Mork (U.S. patent 1,107,222). The solution is to be spun, for example, in petroleum according to Mork, or in alcohol or similar precipitants according to Lederer, or may be treated by the dry spinning process. In the latter case, in consequence of the high boiling-point of acetylene tetrachloride (148° C.) spinning must take place in relatively hot air, and the solution may be diluted with other, more volatile solvents. According to British patent 6554/1909, German patent 237,718, Swiss patent 46,329, U.S. patent 922,340, and French patent 400,652, Fürst Guido Donnersmarcksche Kunstseide- und Acetatwerke dissolve the acetate in highly-concentrated formic acid, and spin the solution (according to German patent 237,599) by extrusion into water, which may conveniently be cooled by ice. According to the process described by Farbenfabriken vorm. Friedrich Bayer & Co., in British patent 28,733/1904, and French patent 350,442, the acetate, in about 15 per cent chloroform solution, is spun in chambers which are heated above the boiling point of the solvent, or it is spun into precipitating liquids such as alcohol, benzene, and so forth. In the same manner, according to French patents 413,787 and

413,671, Dreyfus & Schneeberger spin acetate, obtained with the help of lead chamber crystals as a catalyst, in primary or secondary solution. According to British patent 20,979/1911, Dreyfus spins the acetates soluble in warm, dilute alcohol, obtained according to British patent 20,977/1911, from an alcoholic solution with the addition of castor oil, or the like. According to British patent 16,932/1910, U.S. patent 988,965, and French patent 418,309, Farbenfabriken vorm. Friedrich Bayer & Co. use a mixture of dichlorethylene and alcohol as a solvent, and similarly, according to British patent 13,464/1910, a mixture of pentachlorethane with other solvents such as acetone, chloroform, alcohol, and so forth. According to the process described by Knoll & Co., in German patent 274,260, concentrated salt solutions, for example, solutions of sodium acetate or sodium formate, are used as spinning baths, particularly for primary acetate solutions in glacial acetic acid and also for solutions of the acetate in formic acid. Similar alkaline salt baths are proposed by E. Dammann in British patent 13,872/1914, German patent 287,073, and French patent 473,126. He spins the primary acetate solution into a caustic soda solution saturated with salt, which contains, for example, 20 per cent of NaCl and 5 per cent of NaOH ; or into a sodium hydroxide solution to which sodium acetate has been added ; or in a mixed solution of ammonium acetate and ammonia. It is stated that only a very slight saponification occurs. According to French patent 747,163, W. Vieweg proposes to spin into alkaline baths containing, for example, 25 per cent of ammonia or 20 per cent of sodium hydroxide, which are stated to form satisfactory and lustrous threads, particularly when dextrose, ethyl-alcohol, glycerine, aldehydes or cane sugar are added. It is stated that the spinning process can be carried out very rapidly under such conditions. Chemische Fabrik von Heyden A.-G. claims in British patent 3973/1911, Austrian patent 54,574, Swiss patent 55,344, and French patent 426,436, to obtain particularly rapid coagulation by adding to the cellulose acetate solution a certain quantity of precipitants, such as water, aqueous solutions of bases or salts, alcohol, dilute acids, hydrocarbons and their halogen derivatives, and so forth. We have already described analogous processes in the case of viscose silk (see pages 289 and 290).

A remarkable mixture is described by W. A. Beatty in U.S. patent 1,156,969. He dissolves equal quantities of cellulose acetate and dihydroxy-dimethyl-diphenyl-methane in acetone, and spins into non-solvents such as benzene.

The spinning machinery for acetate silk does not differ in principle from that used for the other varieties and described earlier in this book, and the spinning process itself is naturally quite similar to that for the other varieties. With regard to dry spinning and wet spinning processes we may refer the reader to what has already been stated when considering collodium silk.

Regarding the stretch-spinning process for acetate silk, see German patents 396,702 and 417,988 of Farbenfabriken vorm. Friedrich Bayer and Co., Leverkusen.

For a long period the dyeing of acetate silk met with special difficulties. Further details on this subject and on the properties and use of acetate silk will be found in the corresponding sections, pages 346 *et seq.*, 353 *et seq.* and 367 *et seq.*

CHAPTER XIII

CELLULOSE ETHER SILK

We have still to consider a form of artificial silk of quite specific character also belonging to the group of cellulose derivatives, the future of which is still quite uncertain, namely, cellulose ether silk. It has many promising properties, but on the other hand, many disadvantages—more particularly the comparatively high cost of production—render it doubtful whether this form of silk will achieve technical importance in the future or not. It has not yet been produced in considerable quantity.

Theoretical Considerations on Cellulose Ethers. Ethers in general may be described as oxides of the alcohol radicals or anhydrides of alcohols, produced by the elimination of 1 molecule of water from 2 molecules of alcohol; thus, for example, we may explain the derivation of ethyl-ether as follows—

$$\begin{matrix} C_2H_5 \cdot OH \\ C_2H_5 \cdot OH \end{matrix} - H_2O = \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix} \rangle O$$

Ethyl-ether is a so-called simple ether, as it is produced from two similar alcohol molecules. The two alcohol molecules need not, however, necessarily be the same. When they differ, a so-called mixed ether is formed, such as methyl-ethyl ether from methyl- and ethyl-alcohols, which is constituted as follows—

$$\begin{matrix} CH_3OH \\ C_2H_5OH \end{matrix} - H_2O = \begin{matrix} CH_3 \\ C_2H_5 \end{matrix} \rangle O$$

The cellulose ethers are also mixed ethers, one alcohol in which is cellulose itself and the other, for example, ethyl alcohol. In this case, therefore, we have the following relation—

$$\begin{matrix} C_2H_5OH \\ C_6H_9O_4OH \end{matrix} - H_2O = \begin{matrix} C_2H_5 \\ C_6H_9O_4 \end{matrix} \rangle O$$

As each cellulose molecule $C_6H_{10}O_5$, contains three reactive hydroxyl groups, three series of ether derivatives, the mono-, di- and tri-ethers, are theoretically possible. Actually, further ethers of various stages of alkylation are known, which differ considerably from one another in their solubility and other properties.

Manufacture of Cellulose Ethers. The above equations represent theoretical methods of formation only, and are not equations of reaction for the production of the corresponding ethers. The production of cellulose ethers can be carried out in a manner quite analogous to that of the known organic ethers, either by the interaction of alkyl halides and sodium alcoholate, or by treatment of the alcohol with alkyl sulphate in presence of alkali according to the equations—

1. $C_6H_9O_4 . ONa + ClC_2H_5 = C_6H_9O_4 . OC_2H_5 + NaCl$
2. $2C_6H_9O_4 . OH + SO_2(OC_2H_5)_2 = 2C_6H_9O_4 . OC_2H_5 + H_2SO_4$

In the latter case the sulphuric acid is, of course, neutralized by the alkali which is used.

The technical production of cellulose ethers corresponds to these methods of preparation.

In German patent 322,586, Farbenfabriken vorm. Friedrich Bayer & Co. describe a process for the production of cellulose ethers according to the first of the above equations, after the following remarks with regard to the raw materials: "As a raw material, one may use cellulose in any form, for example, as cotton-wool, filter-paper, wood-pulp, and the like." The description which they give is as follows—

"Cellulose is allowed to gelatinize in strong caustic soda solution (for example, 1 : 1), and preferably for a considerable time (for about 1 to 2 days or longer); the excess of caustic alkali is then removed by pressure or in a centrifuge, and the product is dried either *in vacuo* or by distillation with benzine, petroleum, or the like, until but a small amount of water remains. The sodium cellulose so obtained is heated with 3 parts of ethyl-chloride, calculated on one part of the cellulose originally used, under pressure—with or without stirring—in a closed vessel, for example, to 130° C., for a considerable time,

for example for 8 hours. An excess of ethyl-chloride does no harm. The duration of the heating depends on the temperature, and at lower temperatures the time of heating must be extended. In order to separate the ether which is formed, the excess of ethyl-chloride is distilled off. The residue is extracted with water in order to remove the salts."

The cellulose ether can be purified by dissolving, for example, in alcohol, filtering and reprecipitating, and is so obtained as a white amorphous powder.

A similar procedure is adopted when using other alkyl halides. Ordinarily, 2 molecules of the alkylating agent should be used per molecule of cellulose.

The preparation of cellulose ethers by means of alkali sulphate is due to L. Lilienfeld, and is described in detail in his Austrian patent 78,217/1912.

As a raw material, Lilienfeld uses by preference cellulose products which have been strongly hydrated by solution in any form ; he starts, for example, by warming viscose solution until it is completely coagulated, and thoroughly washing the product ; or from the cellulose hydrate obtained from cuprammonium cellulose solution by precipitation with dilute sulphuric acid ; or, finally, by treating cellulose with strong, 30 to 50 per cent sodium hydroxide solution and precipitating the alkali-soluble portion so obtained with acid ; he dissolves the products obtained by either of these methods in alkali, and treats the solution at raised temperatures with alkyl sulphate, adding a further quantity of alkali if necessary. He states that these various celluloses or cellulose derivatives can also be alkylated in the undissolved condition in the form of more or less coherent pastes. The reaction occurs with evolution of heat and can be carried out either in open vessels or under pressure. By working with correspondingly large quantities of alkylating agent or by repeating the operation several times, highly alkylated products are obtained, which differ essentially from the less highly alkylated products obtained in one operation, or with less reagent, more particularly with regard to their solubility in water. According to the process described in German patent 322,586, which has already been

mentioned, products insoluble in water are alone apparently obtained.

According to German patent 408,342 of E. Teupel, it is advantageous to alkylate in the presence of a small amount of the same salt as that obtained from the alkyl halide and the alkali cellulose during the alkylation process. (See above, equation 1.)

Properties of the Cellulose Ethers. The cellulose ethers are white, amorphous powders which correspond largely in their chemical behaviour to the known organic alkyl and aryl ethers. They are comparatively inert chemically, and are not saponified by water, acids or alkalis, but are decomposed by hydriodic acid with formation of alkyl iodide and regeneration of cellulose hydrate. The less highly alkylated products only are soluble in cold water and in various organic solvents, but are insoluble in hot water. More highly alkylated ethers are completely insoluble in both cold and hot water, but dissolve in most organic solvents. In his patent, above referred to, L. Lilienfeld mentions the characteristic properties of cellulose ethers, as follows—

"The cellulose ethers referred to show an extraordinarily great variety of properties according to the number and character of the alcohol radicles united to the cellulose molecule to form ethers. Some are soluble in water, others insoluble in water and soluble in a number of other solvents. The water-soluble cellulose ethers, so far prepared, show the characteristic property of being soluble in cold water but insoluble or scarcely soluble in hot water, so that their aqueous solutions coagulate or are precipitated on heating. Many of the cellulose ethers which are insoluble in water are soluble in a really surprising number of solvents. Extreme stability and inertness is a common property of them all. They withstand heating to high temperatures in the presence or absence of water and are also very inert to the action of hot alkalis and acids. They are more stable than all simple and mixed cellulose esters and than any reaction products or derivatives of cellulose hitherto described. All cellulose ethers have also in common the properties of plasticity, resistance to chemical and physical influences, and very remarkable hardness and strength of the films, layers, threads, plastic masses and other products

obtained from their solutions or jellies. All these advantages are accompanied by the property of many cellulose ethers, which is not even approximately equalled by any reaction product or derivative of cellulose hitherto known, of dissolving easily and smoothly in an almost unlimited number of solvents. Finally, the cellulose ethers are distinguished by being non-inflammable, or only very slightly inflammable."

The same patent specification also contains the following statements regarding cellulose ethyl-ether—

" It withstands heating for days in an autoclave in presence of water to high temperature, for example, 170° C., without showing any change ; it withstands heating for days with a 25 per cent aqueous solution of sodium hydroxide and also with a 25 per cent alcoholic solution of potassium hydroxide without undergoing any decomposition or change."

Apart from water, the following solvents for cellulose ethers are mentioned : alcohol, methyl-alcohol, glacial acetic acid, formic acid, pyridine, quinoline, picoline, dichlorhydrin, epichlorhydrin, nitro-benzene, methyl-acetate, ethyl-acetate, ethyl-phthalate, ethyl-sebacate, ethyl-citrate, ethyl-succinate, ethyl-tartrate, amyl-acetate, butyl-acetate, ethyl-benzoate, ethyl-laevulinate, acetone, pentachlorethane, tetra-chlorethane, trichlorhydrin, acetylene dichloride, carbon tetrachloride, chloroform, benzene, toluene, xylene, phenol, nitrophenols, ortho-cresol, naphthalene, toluidine, aniline, formanilide, acetanilide, oil of turpentine, camphor, castor oil, linseed oil, Chinese wood oil, olive oil, vaseline oil, paraffin oil, naphtha (petroleum), vaseline, stearine, beeswax, Japan wax, lanoline, nitromethane, phenyl ethers, triphenyl phosphate, tri-cresyl phosphate, and also mixtures of ethyl-alcohol and ether, and ether only, in which, however, the solubility is usually but small.

In the above-mentioned German patent 322,586 of Farben-fabriken vom. Friedrich Bayer & Co., we find the properties of the cellulose ethers in question described as follows: " The cellulose ethers so obtained are produced in the form of colloids. They are insoluble in water, in solutions of alkalis and in dilute acids, but are soluble in most organic solvents, such as alcohol, ether, chloroform, benzene, benzine, carbon tetra-chloride, ethyl acetate, acetone, and the like. Some of the products are only partially soluble in one of the solvents, for example, benzene, according to their method of preparation, whilst the remainder merely swell, and are then only soluble in another solvent, for example alcohol. From their solutions, for

example in benzene, the ethers usually dry in a similar manner to collodium solutions. There remain as residues transparent pellicles, which may be used as films. They do not catch fire, but melt on heating."

Cellulose Ether Silk. For the production of artificial silk, it is obvious that the cellulose ethers which are insoluble in water are alone suitable. It will be realized from the above-mentioned description of their properties that these products may be considered as the ideal raw material for the purpose; more particularly, they possess, to a high degree, exactly those properties which are lacking in the artificial silks so far manufactured, namely, resistance to water and also to alkalis and acids, even at high temperatures. Their ready solubility in so many organic solvents appears to render the cellulose ethers particularly suitable for the preparation of suitable spinning solutions, and for the production of fibres both the wet- and the dry-spinning processes could be considered, as in the case of collodium silk.

It is true that the above-mentioned properties are in themselves not decisive for the suitability of the cellulose ethers for the manufacture of artificial silk on a large scale. The questions as to whether their physical properties, such as lustre, softness, feel, and so forth, correspond to requirements, whether the dyeing of the material may meet with difficulties, and more particularly, whether the production cost may not be too high, are questions all of which apparently still require more or less further investigation. The manufacture on a manufacturing scale was already tried experimentally a few years ago, but the time devoted to this experimental manufacture appears to be relatively short when we remember the prolonged period during which Chardonnet fought for success, and if we also remember that acetate silk, for example, only emerged successfully after experiments extending over more than twenty years. To what ultimate result the experiments with cellulose ethers may lead will only be settled in course of time.

Regarding the manufacture of artificial silk and similar products from cellulose ethers, see, for example, German patents 352,191 and 352,192 (Bayer) and also German patent 342,097 (Sachs).

CHAPTER XIIIa

VARIOUS OTHER FORMS OF ARTIFICIAL SILK

VERY many attempts have been made to produce artificial silk by other methods than those described in the preceding chapters. There were possibilities of three kinds: one could retain cellulose as the ultimate raw material and merely alter the solvent used for producing the spinning solution; one could convert cellulose into other derivatives and use their solutions; or finally, one could choose as a raw material for the threads substances entirely different from cellulose.

All three methods have been attempted and none of them was successful. In the most favourable cases one or the other product was temporarily placed on the market, where, however, it was unable to compete with the tried processes of manufacture of collodium silk, cuprammonium silk and viscose silk, and soon vanished from the scene.

In spite of these facts, these processes are not devoid of interest, and will, therefore, be briefly discussed below.

Unsuitable Cellulose Derivatives or Cellulose Solutions. We must here consider the silks produced from other cellulose esters, analogous to those from cellulose nitrate and cellulose acetate, and also those produced from cellulose with other solvents, analogous to cuprammonium silk.

Cellulose Ester Silks. L. Lederer obtained mixed acetic and nitric acid esters (aceto-nitrates) according to German patents 179,947 and 200,149, by the action of acetic anhydride or acetyl chloride and glacial acetic acid on cellulose nitrate. Regarding the properties of these compounds, see E. Berl and W. Smith (*Ber.*, 1908, page 1839). The production of artificial threads from these esters was described by Lederer in British patent 19,107/1906, German patent 210,778, French patent 368,766, and U.S. patent 1,028,748. An advantageous combination of the properties of both classes of compounds was, up to a point, so obtained, in so far as the threads were more readily dyed than acetate silk and more stable to water than

collodium silk; Lederer attempted to produce a similar combination of properties in another manner, by dissolving both the nitrate and the acetate together in a mixture of acetylene tetrachloride and acetone, or of chloroform and ethyl-acetate, and spinning the solutions. (See German patents 240,751 and 248,559, Austrian patent 42,440, and, French patent 402,072.)

Cellulose formic esters (cellulose formates, formyl celluloses) are obtained according to the process of J. P. Bemberg, A.-G., by treating cellulose with formic acid in presence of sulphuric or hydrochloric acid (British patent 2511/1907, German patents 189,836 and 189,837, French patent 376,262). According to Woodbridge (*J. American Chem. Soc.*, 1909, p. 1067), the statements in these patent specifications are somewhat doubtful. Berl and Smith (*Ber.*, 1907, page 903) also use formic acid and sulphuric acid, but treat hydrocellulose with a mixture of these acids. According to British patent 17,036/1909 German patent 219,163, and French patent 405,293, Nitritfabrik A.-G., Köpenick, obtain cellulose formates by dissolving cellulose in mixtures of formic acid and zinc chloride. Farbenfabriken vorm. Friedrich Bayer & Co., Leverkusen, proceed similarly, according to British patent 24,980/1910, German patents 237,765 and 237,766, and French patent 422,542, by dissolving cellulose in formic acid in presence of sulphuryl-chloride or chlorsulphonic acid, with or without the addition of zinc chloride. Cellulose which has been considerably hydrolysed, for example, cellulose precipitated from solutions, including artificial silk or artificial silk waste, can be dissolved in formic acid alone with formation of formates. This process is used by Nitritfabrik A.-G., Köpenick, according to German patent 219,162, by first dissolving the cellulose in strong sulphuric acid, precipitating, washing, and drying it, and then dissolving it in formic acid. Vereinigten Glanzstoffabriken, Elberfeld, have patented the manufacture of cellulose formate by dissolving artificial silk waste—that is, regenerated cellulose—in formic acid, in British patent 15,700/1910, German patent 233,589, French patent 420,856, Austrian patent 49,177, and patent of addition 60,447.

The formates are unstable in solution. Formic acid has a disintegrating action on the cellulose molecule, and attempts to produce useful threads from these solutions were, therefore, unsuccessful.

The Esters of Higher Fatty Acids have also been proposed for the manufacture of artificial silk, but have hitherto found no technical outlet. Quite apart from the properties of the fibres so obtained, which did not usually correspond to those required of a satisfactory artificial silk thread, the production cost of these compounds was far too high to enable them to compete with collodium, cuprammonium, or viscose silk.

According to Henckel von Donnersmarck's German patent 112,817, cellulose esters of the higher fatty acids are obtained by treating a mixture of cellulose or cellulose hydrate and magnesium acetate with the anhydride of the respective fatty acid. According to Knoll & Co., (German patents 203,642 and 206,950) cellulose esters of fatty acids in general can be prepared by the action of the anhydrides of organic acids on cellulose, or on its nearly related derivatives, in the presence of halogen fatty acids or of neutral salts. Halogen fatty acids, for example, mono-, di-, or tri-chloracetic acid, are also proposed by the A.-G. für Anilinfabrikation for promoting the reaction between cellulose and the anhydrides of fatty acids (German patent 198,482, French patent 368,738); more particularly the cellulose esters of propionic acid and of butyric acid were obtained by the process just described.

Finally, we must here refer to the cellulose esters of aryl sulphonic acids, for example, paratoluene-sulphonic acid cellulose ester, which is obtained, for example, according to German patent 200,334 of the A.-G. für Anilinfabrikation, by the action of aryl sulpho-chlorides on cellulose hydrate.

The Use of Other Cellulose Solvents. We must now consider processes analogous to the production of cuprammonium silk, in which the cellulose is dissolved with the help of other solvents. Such solvents are more especially solutions of salts, various acids, and to a lesser degree certain alkalis.

Zinc Chloride Silk. According to British patent 16,805 1884, Wynne and Powell already utilized the solubility of cellulose in zinc chloride solution in order to obtain cellulose threads from such a solution, which were used for the production of carbon filaments for electric incandescent lamps in place of collodium threads. A very similar process to that of the above-mentioned inventors was patented by Dreaper and Tompkins in their British patent 17,901 1897, German patent 113,786, and U.S. patent 625,033, for producing textile fibres to be used as a substitute for natural silk. In both processes untreated

cellulose was used as a raw material. The only solvent which could be used technically was zinc chloride solution, although in the patent specifications other zinc solutions, namely, the nitrate, bromide and iodide, are mentioned.

The zinc salt solution must be highly concentrated in order that it may dissolve a sufficient quantity of cellulose. Wynne and Powell used a solution of about 40 per cent (sp. gr. 1·8), whilst Dreaper and Tompkins used a solution of sp. gr. 1·85. Solution was carried out at a raised temperature of 90° or 100° C., and spinning was also carried out at a high temperature, for example, at 70° C. Very small amounts of an alkaline earth salt were added to the solutions for the purpose of regulating the solution of the cellulose and increasing the strength of the coagulated threads. The resistance of the threads to water was said to be increased by adding gelatine to the solution, which was hardened by subsequent treatment with formaldehyde. As a spinning bath, alcohol, acetone or a similar liquid, is to be used.

The process described by W. A. P. Werner in British patent 1850/1901 and U.S. patent 697,580, hardly differs from those described above.

By the method just described, a relatively small amount of cellulose only can be dissolved. According to Bronnert, in German patent 118,836, this amounts to 4 per cent as a maximum. This was a great disadvantage, for, as explained on page 69, the concentration of the solution is not without influence on the strength of the thread. A more important point was the considerable hydrating and hydrolysing or depolymerizing effect on the cellulose molecule of the zinc chloride and of the hydrochloric acid produced by hydrolysis of the same, more particularly at fairly high temperatures (see Deming, *Chem. Zentralbl.* 1911, II, page 1435), which causes a deficiency of strength in the thread, particularly in a moist condition. There is also the difficulty that the zinc chloride cannot be completely removed from the thread by washing without the use of acid, for on diluting with water the salt is hydrolytically decomposed, and 20 to 25 per cent of zinc oxide therefore remains in the gelatinized cellulose fibre, and can only be removed by acid.

According to Bronnert, the treatment of the cellulosic raw material proposed by Fremery and Urban in German patent 111,313 (see page 232), which consisted in treating it with oxidizing or reducing bleaching agents before dissolving it in zinc chloride solution, requires a raised temperature. Bronnert himself endeavoured to attain the necessary result without warming by strongly mercerizing the material before or after bleaching (see British patent 18,260/1899, German patents 118,836, and 118,837, Austrian patent 11,066, French patent 292,988, and U.S. patent 646,799). In this manner he certainly obtained more concentrated solutions (about 8 per cent) and somewhat better threads, but even this process did not conform to the requirements which must be demanded of a suitable textile fibre, and the process was not, therefore, technically adopted. The same remarks apply to the process described by Dreaper in British patent 858/1908, according to which raw material pre-treated with sodium hydroxide solution is also dissolved in zinc chloride solution. Thus, the patentee uses hydrated

cellulose, as does Bronnert, and not hydrocellulose, as stated in the patent specification. It is true that at that period these terms were not sharply defined. Dreaper first maintains the solutions in an acid condition, and only renders them alkaline by the addition of zinc oxide shortly before spinning. As a precipitant, he uses alkali hydroxide solution, to which ammonium chloride or ammonia or other materials which prevent the precipitation of zinc oxide may be added; or he uses salt solutions, or finally, also aqueous alcohol. A suitable thread was still less to be expected according to British patent 28,712/1904, of Tompkins and Crombie, who use as a raw material cellulose which has been degraded to hydrocellulose by the action of acid. It is true that hydrocellulose dissolves in zinc chloride solution in comparatively large amount, for example, to a 20 per cent solution, but it then gives a brittle thread of poor quality.

Cellulose Fibres from Solutions of Other Salts. Cellulose also dissolves more or less easily in aqueous solutions of other salts, more particularly of other zinc salts, such as the nitrate and bromide, which dissolve cellulose in a similar manner to the chloride, but not to the same extent. Further solutions which may be used are those of basic lead acetate, calcium bromide, calcium sulphocyanide, potassium iodide, potassium mercuric iodide, barium mercuric iodide and others. According to P. von Weimarn (German patent 275,882), all solutions of neutral salts may be used for the solution of cellulose if the variable factors which depend on the nature of the salt in question, such as concentration, temperature, pressure and time of reaction, are chosen accordingly. However, no process of this kind led to a satisfactory result.

In German patent 353,662, F. Beck proposes to use as a precipitant for such cellulose solutions a strong solution of the same salt as that used for dissolving the cellulose; for example, cellulose may be dissolved in 8.N to 10.N calcium sulphocyanide solution and the solution may be warmed until it has the right degree of fluidity. As a precipitating bath, a cold 60 per cent solution of the same salt may be used, to which small amounts of organic solvents miscible with water, such as methyl- or ethyl-alcohol, acetone and so forth, may advantageously be added.

Solutions of Cellulose in Acids. Strong acids have usually a more rapid and powerful hydrolysing and depolymerizing action on cellulose than the above-mentioned salt solutions. According to the temperature, the duration of the reaction and so forth, degradation products of cellulose are soon formed in the solution, ranging from cellulose-dextrines to glucose:

these cannot, of course, form a satisfactory artificial silk thread. Therefore, no processes in which cellulose is dissolved in strong acids are suitable for the production of artificial silk. Many patents dealing with this reaction have quite other purposes, for example, the manufacture of grape sugar and similar products, as, for example, the process of R. Willstätter (German patent 273,800, French patent 471,479, and U.S. patent 1,141,510), using highly-concentrated hydrochloric acid, and that of Zellstoffabrik Waldhof and V. Hottenroth (British patent 132,815, German patents 306,818 and 363,175, Swiss patents 76,329 and 77,322), according to which ordinary concentrated hydrochloric acid is used with the addition of small amounts of sulphuric acid ; also Z. Ostenberg's process, patented in U.S. patents 1,218,954, 1,242,030, and 1,315,393, according to which, mixtures of acids or of acids and salt solutions are used.

R. Langhans (German patent 72,572, French patent 217,557, U.S. patent 571,530) uses 70 to 80 per cent sulphuric acid, which dissolves the cellulose with formation of sulphuric esters; these are spun to form threads which are decomposed by treatment with water with formation of cellulose hydrate and sulphuric acid. In German patent 82,857/1893, he describes simultaneous or consecutive treatment with sulphuric and phosphoric acids for the production of the cellulose solution. For the same purpose, E. Berl uses strong sulphuric acid containing 60 to 77 per cent H_2SO_4, at a temperature not exceeding $-10°$ C., by which means he believes that he reduces the hydrolyzing effect till it is of no practical importance. According to German patent 227,198/1909, K. Hofmann uses a mixture of phosphoric and acetic acids as a solvent. A mixture of phosphoric and formic acids for the solution of cellulose is claimed by the Vereinigten Glanzstoffabriken in British patent 309/1911, Austrian patent 54,819, Swiss patent 56,146, French patent 424,621, and U.S. patent 1,005,513.

Solutions of Cellulose in Alkalis. The production of artificial silk threads from solutions of cellulose-hydrate in solutions of alkali-hydroxide has been proposed by Vereinigten Kunstseidefabriken A.-G., Frankfurt a. M. in British patent 1750/1902, German patent 155,745, and Austrian patent 20,407. This process was not effective, because the unchanged cellulose molecule (which is not to be confused with the molecular complex) no longer exists, but degradation products only are dissolved, which are unable to form a strong fibre.

Artificial Silk from Non-Cellulosic Materials

In the section on "Raw Materials for Artificial Silk Production," we already became acquainted with the various raw materials other than cellulose, the use of which, for the manufacture of artificial silk, has been attempted (see page 57 *et seq.*). It was already mentioned there that many hopes were based on the use of such substances, more particularly, as were closely allied chemically to natural silk, that is, to fibroin. In view of the lack of success of these attempts, a short survey of the situation will suffice here.

Gelatin Silk. The use of gelatin threads for textile purposes was, of course, only possible if these could be hardened, that is, rendered more or less insoluble in water. Therefore, A. Millar, who worked at this problem for a long period, patented a process for the manufacture of textile fibres from gelatin, in British patent 15,522/1894, German patent 88,225, Swiss patent 12,728, French patent 248,830, and U.S. patent 611,814, according to which the gelatin was rendered insoluble in water by treatment with potassium dichromate or chemicals of similar action, such as alum, tannin, formaldehyde and the like. The concentrated gelatin solution was liquefied by warming, and the thread solidified immediately on being discharged into the cooler air. It was, therefore, impossible to render the threads sufficiently insensitive to water, whilst retaining them in a soft and flexible condition, as these various properties cannot exist together. Moreover, the strength of the threads was very slight, particularly when moist. The product was known as *Vandura silk*, under which name it was marketed by an English company, but very soon disappeared from commerce.

L. E. Jannin proceeded in a similar manner to Millar, using glycerine gelatin according to French patent 342,112. In U.S. patent 712,756 H. Bernstein proposes the use of a mixture of gelatin and silk gum (bas soap) as obtained by boiling raw silk with soap solution. According t French patent 433,956, A. F. Fuchs coagulated gelatin solution wit ammonium sulphate, liquefied the coagulated mass by warming, an spun it to threads which were hardened by potassium bichromate o the like. In German patent 197,250, Austrian patent 40,163, Swis

patent 41,005, and French patent 361,796, Helbronner and Vallée proposed to use ossein, which is closely related to gelatin, for the production of artificial fibres. The ossein is treated with alkali-hydroxide solution at temperatures not exceeding 60° C., and then dissolved in water, alkalis, acetic acid or ammoniacal solutions of metallic oxides. In German patent 202,265, Austrian patent 40,676, and Swiss patent 41,555, the same inventors state that suitable coagulating agents for the ossein solution are neutral or acid metallic salts, alkaline persulphates, tannic acid, sodium chloride to which tannic or oxalic acids have been added, or finally, organic liquids such as alcohol or acetone.

Artificial Silk from the Substance of Natural Silk. A somewhat curious process is claimed by A. Millar in British patent 2713/1897, German patent 93,795, Swiss patent 143,972, and U.S. patent 594,888, according to which the soft parts of dead silk-worms are subjected to pressure by a piston in a cylindrical vessel, and the juice is discharged through a nozzle attached to the vessel and is drawn out to threads. Judging by the economic results, the living silk-worm is more effective. According to German patents 230,394 and 236,907, Baumann and Diesser produce a spinning solution from silk-fibroin by treating the spinning glands of the silk-worm or other portions of the animal body containing fibroin—or even albumen—with formic acid. A better proposal, although it led to no practical result, was that of French patent 354,336 of Soc. an. de la Soie Serret, according to which natural silk waste is dissolved in alkalis, acids, or suitable salts, and then spun. In a similar manner, in French patent 435,156, D. Lance proposes the use of solutions of natural silk waste and the like in cuprammonium solutions or solutions of similar compounds. These solutions are to be precipitated by dilute acids such as hydrochloric acid, to which chlorine may be added in order to produce a bleaching effect. According to British patent 22,753/1907, German patent 211,871, and French patent 382,859, Follet and Ditzler similarly use a solution of fibroin in a solution of the crystals obtained by the action of ammonia on nickel sulphate, copper sulphate or the like. According to French patent 440,846, E. M. S. Galibert uses mixtures of a solution of cellulose in ammoniacal cuprous chloride, and a solution of natural silk in the same solvent. In French patent 441,606 the same inventor also proposes to apply the viscose

process to the substance of natural silk, instead of to cellulose, by pre-treating the silk substance with alkali and then converting it into a mass similar to viscose by the action of carbon disulphide.

Casein Silk. Friedrich Todtenhaupt devoted the long and arduous work of a lifetime, with admirable energy and determination, to the problem of producing artificial silk from casein; this work deserved greater success. (See British patent 25,296/1904, German patents 170,051, 183,317, 203,820, Austrian patent 28,290, French patent 356,404, and U.S. patent 836,788.) The inventor experimented with spinning solutions consisting of solutions of casein in alkalis, in aqueous alcoholic solutions and in zinc chloride solution; as precipitating baths he used dilute acids, solutions of acid salts, and occasionally, for example, in the case of zinc chloride-casein solutions, pure water, alkalis, or organic liquids such as methyl- or ethyl-alcohol. According to German patent 178,985, he also used spinning solutions in which casein solution was supplemented by the addition of viscose or of a solution of cellulose in basic solvents. The fibres were subsequently hardened with formaldehyde. The inventor succeeded in founding the Deutsche Kunstseidenfabrik G.m.b.H., Harburg, for exploiting his process. This firm, however, soon ceased to manufacture, as the product which was marketed did not fulfil requirements and could not, therefore, be sold, as it lacked the soft feel, the necessary flexibility and the required strength.

According to French patent 354,942, Chatelineau and Fleury use casein in an aqueous solution of phenols, whilst H. Timpe (French patent 365,508) stirs casein with acetone and then dissolves it by alkali. According to German patent 275,016, the last-named inventor prevents the fibres produced from casein from becoming hard and brittle after drying. For this purpose he mixes fresh separated milk with concentrated sodium hydroxide solution at the ordinary temperature until it contains 2 per cent of the latter substance, filters from the precipitated horny jelly and precipitates the albumen from the filtrate by means of acids. This latter precipitate is re-dissolved in alkali. The threads spun from the solution are alleged to show increased tenacity if the alkaline solution is treated with about ¼ per cent of a hydrogen peroxide solution before precipitation. According to French patent 403,193 Boistesselin and Gay obtain a material which they call "Caseid," by

dissolving casein in sodium hydroxide solution of 30° to 40° Bé, and precipitating with dilute hydrochloric acid with avoidance of an excess. They prepared from fish bones a product which they called " Fibrisin " ; they freed this from mineral matter with hydrochloric acid, washed with cold water, and treated the product with steam in order to remove the ossein. They then washed with warm water, and treated the product further, as in the manufacture of " Caseid." Solutions of " Caseid " and " Fibrisin " in water were alleged to be very suitable for spinning with the use of strong acids, ferric salts, sodium chloride and so forth, as precipitants. In Baumann and Diesser's German patent 236,907, which has already been mentioned, a solution of albumens in formic acid is proposed for the production of fibres. According to German patent 258,855 of the same inventors, the formic acid solutions are treated with formaldehyde, by which means the elasticity of the threads is considerably increased. According to the statements of Diesser in Austrian patent 63,438, the same purpose is attained by the addition of condensation products of phenol and formaldehyde to the solution of albumen in formic acid. In order to render vegetable albumen, such, for example, as gluten (see page 59), also readily soluble in formic acid, the same inventor first dissolves it in alkali and then precipitates with acid. It is stated that the washed precipitate is then readily soluble in formic acid. According to a process communicated by the Naamlooze Vennotschap Hollandsche Zyde Maatschappy, milk albumen is first decomposed by pyrophosphates and the decomposition product of albumen, which remains in solution, is precipitated alone ; this latter is then converted into plastic form by the addition of alkali or ammonia, either directly or after repeated solution and precipitation. Regarding the production of threads from albumens of various kinds, see also the statements of A. Millar in British patent 6700/1898, Swiss patent 18,042, and U.S. patent 625,345.

Fibres from Vegetable Mucilage and the Like. J. Mugnier proposed the production of artificial fibres from vegetable mucilages of various kinds, such as lichenin, pectin, Iceland moss, agar-agar, and so forth, the flexibility and strength of which was said to be increased by the addition of glycerine, borax, gluten, and so forth. The fibres were to be used more particularly for the production of gauze-like fabrics. The water-soluble ingredients were to be removed after weaving. The fabrics could not be washed, but are said to be sufficiently resistant to atmospheric moisture. (See British patent 9482/1901 and German patent 148,587.) L. Sarason uses alginic acid, which may suitably be dissolved in water to a solution of about 10 per cent, for the manufacture of artificial fibres. He recommends solutions of various metallic salts as a precipitating bath, more particularly solutions of salts of

the alkaline earths ; zinc sulphate, potash alum and sodium bisulphate may also be used. If the alginic acid is dissolved in ammonia, it is stated that aldehydes may also be used as precipitants. (See British patent 21,586/1912, German patent 258,810, Austrian patent 62,968, Swiss patent 59,641, French patent 448,429, and Belgian patent 249,325.) According to the German patent of addition 260,812, better products are obtained if metallic compounds are added to the alginic acid solution, which contain a metal in the anion, for example, molybdates or tungstates.

We may also refer here to the production of fibres from polymerization products of vinyl halides, or of organic vinyl esters, described by Chem. Fabrik Griesheim-Elektron in German patent 281,877 and Austrian patent 70,348.

CHAPTER XIV

THE FINISHED SILK. DYEING ARTIFICIAL SILK

General Considerations. It is not possible in this section to deal with the practice of dyeing artificial silk in any way exhaustively, or to instruct the dyer in the treatment of this material. The number of possible variations in treatment and the number of dyeing formulae and of dyestuffs which can be used is so large that anything approaching a complete description would alone require a large volume. We must therefore content ourselves here with a very general outline of the methods of dyeing artificial silk, which may give the non-specialist some insight into these operations, and afford him a passing view of an artificial silk dye-works.

With regard to all details, we must refer to the references in our summary of the literature, and to the dyeing formulae and pattern cards issued by the various colour works.

As is known to everybody in any way acquainted with the dyeing of textiles, the method of dyeing and choice of dyestuff depend primarily on the character of the material to be dyed. The dyer knows, for example, that acid dyestuffs dye silk and wool, but not cotton, and basic dyestuffs dye silk and wool directly, but cotton only after previous mordanting, and so forth. The various varieties of artificial silk, of which we have discussed the manufacture, also behave very differently with regard to the various classes of dyestuffs, so that it will be convenient to discuss separately the dyeing of each variety of artificial silk.

Generally speaking, we may describe here in advance the dyeing properties of the various varieties of this material. Collodium silk dyes in a similar manner to the animal fibres, natural silk and wool, and thus shows a great affinity for basic dyestuffs, that is, for the salts of colour bases such, for example, as fuchsine, chrysoidin, rhodamine, methylene blue, and so forth; whilst it has relatively very slight affinity for substantive

dyestuffs. Cuprammonium silk behaves towards dyestuffs much in the same manner as mercerized cotton. It is thus easily and directly dyed by substantive cotton dyestuffs, such as benzidine derivatives and the salts of sulphonic acids, but is only weakly dyed by basic dyestuffs, unless the material has previously been mordanted, for example, with tannin and tartar emetic. Viscose silk behaves in a manner intermediate between that of collodium silk and cuprammonium silk ; thus its affinity for basic dyestuffs is rather greater than that of the latter, whereas it shows less affinity for substantive dyestuffs.

We know that all three of these silks consist mainly of cellulose hydrate. The differences in their dyeing properties show that the various differences in the methods of their manufacture also cause differences in composition, which may be relatively very small but are sufficient to influence such sensitive operations as those of dyeing. The behaviour of collodium silk, in particular, may be due, apart from its small content of nitrogen to a more or less considerable admixture of hydro- and oxy-cellulose, which may be due in turn to the hydrolytic action of the strong acids and the oxidizing action of the nitric acid during the nitration process.

In distinction to these cellulose hydrate silks, acetate silk, being an ester silk, occupies a special position, which is also shown by its dyeing properties. Its resistance to water and its very slight powers of gelatinizing in that medium, in themselves cause considerable inertness towards dyestuffs for purely physical reasons, so that special materials and methods have to be used in order to dye this silk, which will be discussed later.

The Dyeing Process. The actual operation of dyeing artificial silk does not differ from that used for other textile materials. By far the greater portion of artificial silk is dyed in hank form in ordinary troughs or vats which are directly or indirectly heated by leaden tubes, and in which the hanks are dipped on glass rods or tubes or on smooth wooden rods. The glass rods should not have a rough surface ; when wooden rods are used these must be smooth and free from splinters, as must the walls

of the wooden vats. Owing to the sensitiveness of the fibre, it must be handled in the dye-bath with great care and attention, and the same remarks apply in this case as were made on page 157 in connection with the mechanical after-treatment. As in the case of cotton, natural silk and so forth, the hanks are repeatedly turned in the dye-bath, as otherwise the portion which is immersed in the vat for a longer period is dyed more deeply. More particularly it is advisable to turn the hanks rapidly several times before finally removing them from the bath. Owing to the sensitiveness of the artificial silk thread, steps are naturally taken to conclude the whole dyeing operation as rapidly as possible, and the actual dyeing process does not usually last longer than one-half to three-quarters of an hour.

Dyeing in apparatus in which the goods are tightly packed and the dye-bath is circulated through the material under pressure—usually by compressed air—a process which is much used for the dyeing of cotton and wool and which avoids damage to the material, has not proved particularly satisfactory for artificial silk, and is only used here and there for finished products, such as embroidery, lace, and so forth. Regarding special dyeing apparatus for artificial silk, see German patent 225,313 of E. Dierichs and German patent 219,074 of E. Esser.

Piece goods are dyed on the jigger, or in the winch dye beck, in which the fabric is continually carried through the dye-bath by rotating rollers or reels.

The water used for the dye baths should be pure and as soft as possible. Hard water is boiled with soda and the precipitated lime sludge is removed.

The goods are always previously wetted, and are then frequently introduced into the cold bath which is gradually warmed ; sometimes they are first introduced into a completely exhausted bath. Formerly in particular, when artificial silk was still more sensitive than to-day, too long an exposure of the silk to the hot bath and too high a temperature were avoided as far as possible. In many dyeworks the goods are now immediately entered into the almost boiling dye-bath.

The temperature is usually adjusted according to the desired depth of shade, temperatures of 40° to 50° C. being ordinarily used for lighter shades, about 60° C. for medium shades and 70° to 80° C. for deep shades.

Apart from mordanting and so forth, no pre-treatment of artificial silk is usually undertaken before dyeing. Sometimes the silks are mechanically cleaned before entering them into the dye-bath in the case of very light shades. In some dye-works the goods are pre-treated with soda and soap, for example, with a solution of 4 per cent of soda and 8 per cent of Marseilles soap for half an hour at 80° C. ; they are then rinsed warm and then cooled, dipped into 8 per cent hydrochloric acid and again rinsed.

In order to achieve rapid dyeing and as complete an exhaustion of the bath as possible, acids or salts may be added. The addition of bast soap, gelatin, glucose, starch or similar protective colloids, prevents the precipitation of the base, developer, or dyestuff from the solution by the addition of salt. Turkey-red oil, Monopol soap, and similar compounds exert a levelling effect, that is, uniform deposition of the dyestuff on the fibre.

The goods, which have been completely dyed and, if necessary, shaded off, are rinsed, usually in the cold, and then carefully dried in a centrifuge. Any twisting or wringing is to be avoided. Drying is carried out at a moderate temperature, preferably in hot-air drying chambers (see pages 154–155).

Dyestuffs. Regarding dyestuffs, basic and substantive dyestuffs are more particularly used, in accordance with the above summary, but sulphide dyestuffs, azoic or developed colours, and latterly, the very fast indanthrene dyestuffs, are also used. The latter are vat dyestuffs which are dyed in a similar manner to indigo, the dyestuff being reduced to a colourless leuco-compound by a hydrosulphite in an alkaline bath, and fixed on the fibre as such. The dyestuff is then formed on the fibre by subsequent oxidation in the air. In practice three main methods of dyeing indanthrene dyestuffs are distinguished. The I.N. process consists in dyeing at 50° to 60° C. without the addition of salt ; the I.W. process in

dyeing at 45° to 50° C. with the addition of salt ; and the I.K. process in dyeing with double the amount of salt at the ordinary temperature of 25° to 30° C. According to G. Rudolph (*Die Kunstseide*, 1925, page 147), indanthrene dyestuffs are of particular importance in the case of artificial silk, as by their means both yarns and piece goods can be dyed to produce results extremely fast to washing, which are also very fast to light if the dyestuffs are rightly chosen. They are also always fast to topping.

The substantive dyestuffs offer the advantage, apart from simple methods of dyeing, that they usually give results on artificial silk which are very fast to washing and light and better than those obtained with basic dyestuffs.

Hundreds of suitable dyestuffs of the various classes are available, and a list even of the more important would be too long to be inserted here.

With regard to the conditions of dyeing, the substantive dyestuffs are dyed, as in the case of cotton, from a hot aqueous solution, with the addition of salt (sodium chloride or Glauber salt), whilst the basic dyestuffs are usually dyed from a hot bath acidified with acetic acid. When using many basic dyestuffs the goods are first mordanted in order to increase the fastness of the dyeing. The best mordant is tannin-tartar emetic mordant. The silk is, for example, first treated with a cold dilute solution of tannin for 10 to 15 hours, is then centrifuged and treated with a solution of tartar emetic ; or the goods are immersed in a warm bath of tannic acid, slightly acidified with hydrochloric acid, for 2 to 3 hours, then turned several times, centrifuged and treated with a 1 to 2 per cent solution of tartar emetic. Antimony tartrate is thus deposited on the fibre and fixed, and forms a lake with the dyestuff. Piece goods are impregnated with the solutions on the slop-padding or Foulard machine, in which they are stretched over suitably arranged guiding rollers and carried through the solutions whilst fully extended.

Sulphide dyestuffs are dyed from sodium sulphide solution, with addition of soda, as in the case of cotton. In German patent 409,105 the Höchster Farbwerke propose to dye

sulphide dyestuffs in the same manner as vat dyestuffs by reducing them with hydrosulphite and alkali-carbonate, and to dip the artificial silk into this vat, which is free from caustic alkali. R. Clavel's German patent 415,937 should also be referred to here.

Ice colours (developed colours), vat dyestuffs and so forth are also used for artificial silk in exactly the same manner as for cotton or wool.

Eosins may conveniently be dyed in a neutral salt bath ; Methyl Blue, Pure Blue, and Water Blue, with the addition of alum ; Isamine Blue, Titan Como and similar colours in an acetic acid bath.

Acid dyestuffs are occasionally used, particularly for collodium silk, usually with the addition of aluminium acetate, but do not always give favourable results.

Additions to the dye-bath and subsequent development, such as after-chroming, coppering, and the other practical dyeing operations, may all be used for artificial silk in the same manner as for other textile fibres. The fact that the individual artificial silks differ from one another in their dyeing properties and also from the other textile fibres, naturally affords opportunity for the production of interesting effects, such as reserve effects, when dyeing mixed fabrics, making use either of the fact that the various fibres dye in a different manner or, in the case of multiple bath processes and topping, that many colour effects may be obtained. Such artificial silk effects play an important part, particularly in the case of woollen fabrics. In these cases, of course, the artificial silk must be dyed very fast (fast to acid boil and fast to washing) in order that it may not suffer during the numerous further operations which the goods undergo.

Dyeing Collodium Silk. Basic dyestuffs are used by preference for dyeing collodium silk, as might be expected from the relatively great affinity of this silk for these dyestuffs, which has already been referred to. Dyeing is always carried out in an acetic acid bath, in which the goods may be directly dyed without mordanting, particularly if such basic dyestuffs are chosen as dye unmordanted cotton fairly strongly, such as

Diazine Black and Diazine Green of Kalle, Janus Black of Höchst, and so forth. Such direct dyeings are not usually particularly fast. When greater fastness is required, the fibre should first be mordanted, preferably with tannin and tartar emetic, as already described. The fastness may also be appreciably increased by after-treatment with tannin or tannin and tartar emetic. Collodium silk is usually similarly mordanted if it is to be dyed with substantive colours, but this is not always necessary and depends on the desired shade and degree of fastness. Broadly, the same methods are used with these dyestuffs as are used when dyeing cuprammonium or viscose silk. (See below.)

Dyeing Cuprammonium Silk. This material can only be directly dyed with basic dyestuffs if weak shades are desired, whereas for fuller shades previous mordanting with tannin and tartar emetic is necessary. In far the larger number of cases, however, substantive dyestuffs are used. The material is dyed in exactly the same manner as cotton, with the addition of soda or common salt, or Glauber salt, at temperatures of 30° to 40° C. for light shades and 60° to 70° C. for heavier shades. As in the case of cotton, the addition of Turkey-red oil, Monopol soap or similar products has a favourable influence both on the shade and on the uniformity of dyeing. The goods are frequently topped with basic dyestuffs, usually in a cold bath, with the addition of acetic acid. By after-treatment with solutions of formaldehyde, copper sulphate, potassium bichromate, chrome alum, and so forth, the fastness to washing and light of the dyeings may be considerably increased. Avivage, which is still frequently used, and for which oil emulsions are usually employed, usually produces a clearer, purer, and deeper colour, increases the lustre and gives the material a soft feel.

Many substantive dyeings on artificial silk may be subsequently diazotized in the manner well-known to every dyer, and developed with naphthol or similar products ; or they may be developed directly with diazo solutions, for example, with diazotized p-nitraniline. The diazotizing process is especially used for deep, fast black, dyeings.

Sulphide dyestuffs are dyed on cuprammonium silk from an aqueous sodium sulphide solution with the addition of soda, as in the case of cotton, but in the case of artificial silk somewhat larger quantities of sodium sulphide are usual, by which means a more uniform dyeing of the material is attained.

Dyeing Viscose Silk. In the case of this silk, what has above been stated regarding the dyeing of cuprammonium silk also holds, always remembering the fact, which has already been referred to, that substantive dyestuffs have less affinity for viscose silk than for cuprammonium silk, but that basic dyestuffs, on the other hand, are dyed somewhat more easily. Therefore, in the case of substantive dyestuffs the temperature can usually be increased slightly for this material, and for dark shades, for example, may be 80° to 90° C., whilst in the case of basic dyestuffs less dyestuff, more dye-bath and a shorter time or lower temperature are required.

In German patent 360,001, Höchster Farbwerke propose to dye viscose silk in the freshly-spun condition with leuco-compounds of sulphide or vat dyestuffs, as has also been proposed for acetate silk. The process has, however, not been much used in practice. In German patent 371,412, E. Schülke proposes to dye viscose silk immediately after washing, that is, without further after-treatment such as desulphurization, bleaching and dyeing.

Dyeing Acetete Silk. This proved to be a very difficult material, as owing to the fact that it scarcely absorbs any water, it offered so much resistance to dyeing that for a long period attempts were made in vain to find suitable materials and methods for dyeing this silk satisfactorily in any shade. Acetate silk possesses a certain degree of affinity for basic dyestuffs only, but even this is not nearly sufficient to satisfy commercial demands.

These difficulties have now been practically overcome and cellulose acetate silk can be dyed in any desired shade just as other artificial silks.

There were three possible methods of achieving this result. Greater affinity for dyestuffs could be imparted to the acetate silk by special treatment, or special dyeing methods could be

developed or, finally, special dyestuffs could be selected or invented for this particular purpose. All three methods were attempted and were all successful, but to varying degrees.

The most obvious, and probably the first method which was attempted, was the superficial saponification of acetate silk by caustic alkalis. This was carried out very simply, for example, according to British patent 175,486 of the British Celanese Co. by turning hanks for about $\frac{3}{4}$ hour at 75° C., in a bath containing 30 per cent of NaOH, calculated on the weight of the silk, after which the goods were well washed. By this means the surface was converted into cellulose hydrate in consequence of separation of the acetyl groups, and thus attained the same affinity for colours as other artificial silks. See also H. S. Mork's British patent 20,672/1910 and U.S. patent 1,074,092. The silk which has been pre-treated in this manner is then dyed in approximately the same manner as viscose silk, but the temperature is not raised above 70° to 75° C., as water has also a saponifying action at high temperatures and would, moreover, damage the lustre of acetate silk. In this manner quite satisfactory dyeings are obtained.

This process represented a considerable advance but had many disadvantages. More particularly the pre-treatment with caustic alkali was not easy and had to be carried out with great care, as if the saponification was carried too far, not only were the lustre and strength of the fibre reduced, but its most valuable property, namely, the relatively high resistance to water as compared with other artificial silks, was also impaired. Moreover, the loss of the acetyl groups also naturally led to a loss of weight. According to Lawrie (*Faserstoffe und Spinnpflanzen*, 1924, page 37), the loss is always approximately equal to the weight of caustic soda which is used. Moreover, the dyeing was naturally very superficial only, and the more superficial, the less the fibre was attacked during the pre-treatment.

Saponification may also be carried out simultaneously with the dyeing process by adding caustic alkali to the dye-bath. According to German patent 350,921 of the Soc. des Usines du Rhône, the simultaneous addition of salts or colloids, together with the alkali, has a very favourable effect in this

case. According to the process of the Badische Anilin- & Soda-Fabrik the saponification may with advantage be carried out with lime or barium hydroxide in presence of formaldehyde.

Further, according to German patent 398,583 of W. Marshall, strong caustic alkali solution containing 21 to 27 per cent, such as is used for mercerization, does not attack acetate silk when applied for a short period below 15° C., and the process described in the patent is founded on this fact. The process is described in greater detail on page 373.

The firm of Knoll & Co. replace the permanent alteration of the surface of the fibre by the saponification process by a temporary gelatinization of the fibre, which is stated also to cause a considerable increase in its affinity for dyestuffs. The gelatinization is said to be achieved, according to German patent 199,559, by treatment with dilute organic solutions or solvents, for example, with 50 per cent aqueous alcohol, dilute acetic acid, aniline, ether, and so forth ; or according to French patent 10,783 and the addition to German patent 383,636, by treatment with solutions of organic acids. (See also German patent 234,028 and U.S. patent 1,002,408.) We must also refer to German patent 228,867 of Fürst Guido Donnersmarckschen Kunstseiden- u. Acetatwerke, according to which cellulose acetate may be dyed with the help of acetin or other water-soluble glycerine or glycollic esters or derivatives of the same, by incorporating these compounds with the silk during its manufacture or by adding them to the dye-bath during dyeing. All these processes are relatively expensive and their effects are incomplete.

We already mentioned at the beginning of this section that acetate silk shows a certain affinity for basic dyestuffs and thus approximates in its behaviour to animal fibres. In fact, quite good dyeings can be obtained with certain basic dyestuffs such as malachite green and brilliant green, without preliminary mordanting. The dyeing takes place in an acetic acid bath with an abundant addition of common salt, and is carried out in about ½ hour at 70° to 75° C. After rinsing well with lukewarm water the goods are soaped in a lukewarm bath for 5 to 10 minutes, rinsed again, then soured with dilute acetic acid

and finally well washed. In order to remove all impurities from the surface of the fibre some dyeworks treat the silk, before entering it into the dye-bath, in a lukewarm soap bath with addition of some ammonia for about $\frac{1}{4}$ hour and then wash well with the addition of a little Monopole soap or Turkey-red oil. It is stated that the dyeing process is very favourably effected by this treatment.

Moreover, various acid dyestuffs, such as Alizarin Yellow, Anthracene Blue, Metanil Yellow, Alizarin Orange and Cloth Red can also be used for acetate silk in the same manner as the basic dyestuffs.

According to communications of J. Besançon (*Die Kunstseide*, 1925, page 121) it is possible to dye acetate silk with all basic dyestuffs after a preliminary treatment of the silk with "Acetanol N," which is sold by the Kuhlmann Works (Cie. Nationale des Matières Colorantes et Manufactures de Produits Chimiques du Nord Réunies). The silk is treated with the undiluted product, the excess of which can be repeatedly used after centrifuging. The process is said to be very simple to operate. The thoroughly degreased silk is treated for 20 minutes in a warm Acetanol bath at 30° to 40° C., centrifuged, washed, and then dyed for 20 to 30 minutes directly in the dye-bath, which has been slightly acidified with acetic acid.

A similar effect is obtained by "Celloxan," a product sold by Farbenfabriken vorm. Friedrich Bayer & Co., which is also said to enable acetate silk to be dyed with basic dyestuffs. According to L. G. Lawrie (*Faserstoffe und Spinnpflanzen*, 1924, page 38) this compound appears to consist mainly of zinc nitrate. (See German patent 412,819.) Such salts have often been recommended; for example, Höchster Farbwerke propose the use of ammonium salts, and according to the statement in R. Clavel's British patent 182,830, the affinity of acetate silk for basic and mordant dyestuffs is considerably increased by the addition of magnesium chloride, stannous chloride and so forth. According to German patent 415,681 of the Badische Anilin & Soda-Fabrik, the absorptive power of cellulose esters is increased by treating the esters before or during the dyeing process with the esters of inorganic oxy-acids or with salts of such esters, for example, with potassium ethyl sulphate, sodium dicresyl-phosphate and so forth.

Among special dyeing methods there may be mentioned a specific application of developed colours. According to British patent 24,284/1907, German patent 198,008, and French patent 383,636, Knoll & Co. have found that amines, phenols and derivatives of the same are absorbed by acetylcellulose from dilute aqueous solutions and that in this

manner solid solutions of the above-mentioned compounds in acetyl-cellulose can be obtained, which may be used in the well-known manner for the production of dyes on the fibre, for example, by diazotizing and coupling, and so forth. Among numerous patents relating to this subject we may select as an example the recent German patent 413,611 of R. Clavel, in which four different methods of carrying out the above-mentioned principle are described. According to this patent, acetyl-cellulose can be dyed with a base and a developer in one bath and the absorbed base may be diazotized in a second bath. On the other hand, the base may first be absorbed alone, then diazotized on the fibre in the same bath and coupled with a developer in a second bath. The third variation consists in absorbing the base in the first bath, then diazotizing it in a second bath, and finally coupling with the developer in the same bath. Finally, the developer may be absorbed in the first bath, whilst in a second bath the base is first absorbed and finally diazotized in the same bath. See also German patent 418,940 (Bayer & Co.)

A process which has apparently proved satisfactory is the " dispersion dyeing " of the British Celanese Co. This process is based on the observation that certain dyestuffs form highly dispersed colloidal solutions in Turkey-red oil and similar compounds, in some cases in the cold, and in some cases on warming, and that extremely fast dyeings are obtained on acetate silk with these solutions. Dyeing is carried out in the usual manner with the addition of salt, particularly for deeper shades. When ordinary Turkey-red oil is used as a dispersing agent the dyeing is carried out in a neutral or alkaline bath but in an acid bath when highly-sulphonated castor oil is used. Only such dyestuffs can be used by this method as show a direct affinity for cellulose acetate. The " Dispersol " process of the British Dyestuffs Corporation, Ltd., is very similar.

According to British patent 204,280 of the Badische Anilin & Soda-Fabrik bisulphite compounds of insoluble or slightly soluble azo-dyestuffs are used for dyeing acetate silk.

It is also said to be possible to dye acetate silk from baths in which the dyestuffs are not dissolved but merely suspended. This appears

however, to be a very doubtful process and not capable of extended application, although one or another dyestuff may perhaps yield satisfactory dyeings. According to British patent 179,384 of W. Harrison and B. Ledward & Co., this is the case if protective colloids are added to the dye-bath.

With regard to the selection or production of special dyestuffs for acetate silk, R. Clavel in particular has communicated details on experimental results. According to his observations acetate silk can only be directly dyed with dyestuffs containing active groups (OH, NH_2, NO_2, and so forth), in the molecule but not sulphonic groups ; or in which any sulphonic groups which may be present are neutralized by a larger number of active groups (see British patents 182,830 and 182,844, and German patent 355,533). According to British patent 202,157 of the British Dyestuffs Corporation, Ltd., the lack of affinity of dyestuffs containing one sulpho-group can be neutralized by rendering aminoazo-, substituted aminoazo- and similar dyestuffs containing sulpho-groups soluble, by the introduction of carboxyl groups.

German and other colour firms market a whole series of dyestuffs for acetate silk under various names, the constitution of which usually agrees with Clavel's rule, at any rate in so far as they act as direct dyestuffs. We may mention here, for example, the Azanyl dyestuffs of Höchster Farbwerke ; the Azonine dyestuffs of Cassella & Co. ; the Cilia dyestuffs of Soc. pour L'Industrie Chemique ; the Ionamine and Cellutile dyestuffs of A. Green and the British Dyestuffs Corporation, Ltd. (See also German patent 395,636.)

Acetate silk can also be dyed in the usual manner by indigo and by sulphide dyestuffs, but as little alkali as possible must be used in order to avoid serious attack of the fibre through saponification. (See, for example, German patent 415,937 of R. Clavel.)

It is said that aniline black can be satisfactorily dyed on acetate silk.

With regard to fastness, particularly to light, it is interesting to note that dyestuffs often behave quite differently on acetate silk to their behaviour on other fibres. Similar observations can be made with regard to fastness to water and to washing.

The fastest dyestuffs on acetate silk are usually those obtained by developing bases. (See the communication of E. Müller, *Faserstoffe und Spinnpflanzen*, 1924, page 15.)

If mixed fabrics consisting of acetate silk and cotton are to be dyed, the latter can be dyed in the usual manner with substantive dyestuffs which have no affinity for acetate silk, and the former can then be dyed with such basic dyestuffs as do not dye cotton. (See, for example, German patent 152,432 of A. Wagner.) The dyeing of acetate silk mixed with wool is somewhat more difficult, but it is said that this can be carried out satisfactorily by means of the above-mentioned dispersion dyestuffs.

The printing of acetate silk fabrics can be carried out comparatively easily by the saponification process. The material is printed with a paste containing caustic alkali and is then dyed with dyestuffs which have no affinity for the unchanged acetate silk, but which are fixed by the surface where it has been saponified by the alkali.

It should be added that successful attempts have been made to dye cellulose acetate before spinning by adding the dyestuff to the spinning solution, by which means coloured cellulose acetate threads are obtained if the dyestuff has been suitably chosen. B. Borzykowski adds the dyestuff to the acetylation mixture, that is, to the acetic anhydride and glacial acetic acid, and then adds the cellulose to the heated mixture. (Swiss patent 60,510, French patent 444,588, U.S. patent 1,041,587.) These dyeings are often, however, deficient in fastness, and these processes have lost in importance since the direct dyeing of acetate silk has been carried out without special difficulty.

CHAPTER XV

PROPERTIES OF ARTIFICIAL SILK PHYSICAL AND CHEMICAL

Lustre. If we consider artificial silk in general and compare its general appearance with that of the other textile fibres, we are at once struck with the extraordinary lustre of the artificial product, which may greatly excel that of natural silk. The intensity of the lustre is naturally dependent on the particular method of production, and is varied deliberately according to the use for which the material is intended.

But the character of the lustre also varies within fairly wide limits, and is definitely different for the various varieties of artificial silk. The lustre of collodium silk is strong, lively, and rather flickering ; that of cuprammonium silk, bright and glossy ; whilst viscose silk has a soft, silvery lustre. The lustre of acetate silk is also somewhat soft but at the same time somewhat flickering, like that of collodium silk. The lustre of Vandura silk (gelatin silk) is, according to Knecht (*Lehne's Färberztg*, 1899, page 90), just as beautiful as that of natural silk, but is said to have a very restless flicker when illuminated.

The degree of gloss can be determined optically by so-called gloss-meters, which are sold, for example, by the firm of Goerz in Berlin. (See also *Faserstoffe und Spinnpflanzen*, 1922, pages 1, 35, and 87.)

Colour. The colour of unbleached or undyed artificial silk also varies with the variety of silk ; collodium, cuprammonium and acetate silks usually show a very bright bluish-white colour, whereas that of viscose silk is usually somewhat yellowish. In this case also, however, the colour of the product often varies within wide limits, even when made by the same method.

Handle. The handle of the material depends even less on the variety of the silk than its lustre and colour, but is, on the contrary, more particularly dependent on suitable after treatment, such as soaping, souring, glossing, and so forth,

as we already mentioned in the General Section. When the spun material possesses the other necessary properties, which may naturally be assumed, it is not difficult to endow it by such means with a soft but full feel, corresponding to the grip of natural silk. The thickness and number of the individual filaments and the degree of twist are factors which also contribute to the character of the feel. The handle is softer, the finer and relatively more numerous the individual threads and the less the twist, that is, the number of turns per metre length.

Micro-structure of Artificial Silk. The statement of R. O. Herzog and Jahnke (*Ber. d. chem. Ges*,. 1920, page 2162), that artificial silk is distinguished from natural cellulose fibre by the fact that the crystallites are not arranged in a definite manner, has been found to be incorrect according to a later communication by Herzog and Gonell (*Kolloid-Zts.*, 1924, page 201). It has been found that all artificial silks, with the exception of acetate silk, when examined by Röntgen rays show the diagram of a crystalline substance, and the measurements show that the diagrams of artificial silks correspond, with regard to the position and intensity of the interference, with the diagram of mercerized cellulose, so that it may be assumed that the crystalline substance of mercerized cellulose is contained in artificial silks.

Specific Gravity. Whilst the specific gravity of natural silk is 1·4, that of the various artificial silks varies from about 1·3 to 1·55, being thus 10 per cent higher than that of the natural product. An exception is formed by Vandura silk, the specific gravity of which is given by Hassack as 1·37 (*Österr. Chem. Ztg.* 1900, page 269), which is not surprising, as this silk consists of gelatine. (See also Silbermann, *Die Seide*, 1897, Vol II, page 148, and Herzog, *Lehne's Färberztg.*, 1894–5, page 49.)

Thickness and Cross-section of Fibre. The thickness of individual fibres is a very variable factor, which, together with the number of individual fibres determines the thickness of the main thread, and therefore the titre or number of deniers. The thickness of the thread is, therefore, not a characteristic either of artificial silk in general or of the individual varieties of this material, in contrast to the position with other fibres

and more particularly with natural silk. It can only be said in general that formerly the fineness of the natural silk fibre, the thickness of which is about 15μ, was not attained by any of the various varieties of artificial silk, the thickness of which was in general between 30 and 40μ. This is, however, no longer true. The finest individual artificial silk fibres obtained, for example, by the stretch-spinning process, are of 1 to 2 deniers, and these exceed natural silk in fineness, having a thickness of about 10μ only. (Regarding the term " denier " see pages 160–161.)

The thickness of the fibre depends, however, very considerably on the degree of moisture, and therefore, on the dampness of the air, and, under the microscope, on the character of the medium in which it is embedded. Further details on this subject will be found in the section on " Water Contents," page 364. (See also, A. Herzog, *Unterscheidung der natürlichen und künstlichen Seiden*, 1910, page 32.)

Very interesting observations have been made by Herzog (*loc. cit.*, page 34) on the uniformity of the fibre thickness. He expressed the unevenness in percentages of the arithmetical mean and found it to be higher in the case of collodium silk, namely, 37·7 for Chardonnet silk and 29·4 for Lehner silk. He found it to be 14·6 for viscose silk, 7·6 for Glanzstoff (cuprammonium) silk, 4·1 for gelatin silk, and 3·0 for acetate silk.

The shape of the cross-section of the individual fibres is usually characteristic not only of the particular variety of artificial silk, but frequently, according to E. Bronnert, even of the special method of operating one and the same process, and more particularly of the character of the coagulation. (See A. Herzog, *loc. cit.*, page 23 *et seq.*, also Süvern, *Kunstliche Seide*, 1921, page 646.)

Figs. 88 to 90 show several typical cross-sections of various artificial silk threads, namely, denitrated collodium silk, Fig. 88 ; cuprammonium silk, Fig. 89 ; and viscose silk, Fig. 90 ; all three according to A. Herzog (*loc. cit.*, pages 23-24). Similarly, Fig. 91 shows a cross-section of viscose silk when spun into sulphuric acid, into sulphuric acid and salt

(but without excess of neutral salt) or into a weakly acidified ammonium sulphate solution ; Fig. 92 shows viscose silk from mineral acid, with a considerable excess of neutral salt (according to Süvern, *loc. cit.*, page 644) ; Fig. 93 shows cross-section of the fibres of modern acetate silk (according to A. Herzog, *loc. cit.*).

All these sections are magnified 230 times.

On cross-sections of collodium silks in particular, see the communications of Chardonnet (*Rev. Générale de l'Industrie Textile*, 4th year, Vol. IV, pages 9 and 10).

Strength and Extensibility. The absolute strength of the thread naturally depends on its thickness, that is, on its titre, also on the degree of twist, but without being necessarily proportional to these factors. The composition of the substance of the thread is, of course, of primary importance. In order to compare the strengths of various products the figures for the absolute strengths are frequently calculated for 100 deniers. The normal strength is then on the average about 30 per cent greater than the titre, so that a given thread of 100 deniers should show a breaking strain of about 130 gm. As, however, as already mentioned, the strength is not necessarily proportional to the thickness, it is safer always to give both the actual figure for the strength and the titre. Occasionally the strength figure is simply divided by the titre, so that the strength is calculated for a thread of unit titre.

The strength is also frequently given in terms of kilograms per sq. mm. cross-section, or sometimes, as in the case of paper, the " breaking length " of the fibre is stated, that is, the length of fibre which weighs as many kilograms as correspond to the breaking strain, or, in other words, the length of fibre which would just break under its own weight. Older figures on the breaking length of artificial silk were given, for example, by Schlesinger (*Papier Ztg.*, 1895, pages 1578 and 1610). He obtained, among others, the following figures—

	Breaking strain
Trame silk, air dried . . .	21,465 m.
„ „ moist . . .	5,076 m.
Artificial silk, air dried . . .	9,971 m.
„ „ moist . . .	1,020 m.

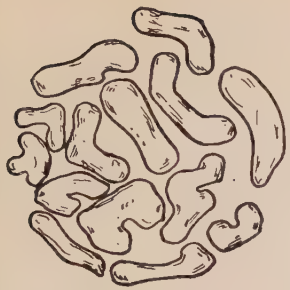


Fig. 88. Denitrated Collodium Silk
Magnification 230

Fig. 89. Cuprammonium Silk
Magnification 230

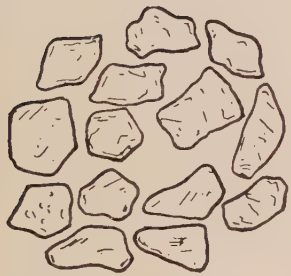


Fig. 90. Viscose Silk
Magnification 230

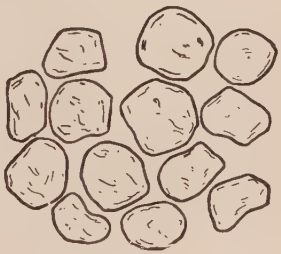


Fig. 91. Viscose Silk Spun in Acid Solution
Magnification 230

Fig. 92. Viscose Silk Spun in Acid Solution with Large Excess of Neutral Salt
Magnification 230

Fig. 93. Acetate Silk
Magnification 230

Formerly, the breaking strain of artificial silk was only about one-fourth that of natural silk, namely, 0·7 to 0·8 gm. per denier, compared with 2·1 to 2·3 gm. for natural silk. To-day a very much better material is usually manufactured. The strength of viscose silk, for example, is usually about two-thirds that of natural silk, namely, about 1·4 gm. per denier.

As will be clear from the above figures, the strength of the artificial silk thread in the moist condition is usually greatly reduced, in consequence of gelatinization, and to a much greater degree than is that of natural silk. The strength in a moist condition is usually only 10 to 30 per cent of that in the dry condition, except in the case of acetate silk, whilst in the case of natural silk, on the other hand, the strength when moist is about 80 per cent of the dry strength. Thus the loss in strength on moistening ordinary artificial silk is about 70 to 90 per cent. According to older figures of R. W. Strehlenert (*Chem. Ztg.*, 1901, page 1100), the following results were found for the artificial silks at that date. They are given in kilograms per sq. mm.—

	Dry	Wet
Natural silk—		
Raw Chinese silk	53·2	46·7
Raw French silk	50·4	40·9
„ „ „ boiled off and glazed	25·5	13·6
„ „ „ dyed and weighted	20·0	15·6
„ „ „ 110 per cent weighting	12·1	8·0
„ „ „ 140 „ „ „	7·9	6·3
„ „ „ 500 „ „ „	2·2	—
Chardonnet silk	14·7	1·7
Lehner silk	17·1	4·3
Strehlenert silk (see pages 11, 108 and 110)	15·9	3·6
Glanzstoff Elberfeld, undyed	19·1	3·2
Viscose silk (Cross and Bevan)	11·4	3·5
More recent viscose silk	21·5	—
Cotton yarn	11·5	18·6

P. Krais (*Textilindustrie*, 1924, page 43), communicates the following figures—

	Fineness in deniers	Breaking load in grms.		Loss per cent
		Dry	Wet	
Cuprammonium silk	1·4	3·3	2·4	27·3
Viscose silk	5·3	12·4	6·1	50·8
Viscose silk	8·1	18·9	9·3	50·8
Viscose silk	3·0	7·4	5·2	29·7
Nitrate silk	5·9	11·4	6·0	47·3
Nitrate silk	8·2	22·7	12·9	43·3
Acetate silk	5·0	7·9	6·6	16·4
Natural silk, degummed	1·27	7·8	7·3	6·4

It is remarkable that, as the table shows, finer threads are relatively stronger, and we will note the same phenomenon when considering the strength of thicker threads, such as artificial horsehair, and so forth (see page 382). P. Krais (*loc. cit.*, page 10) calls attention to the importance of giving details regarding the fibre and the conduct of the determinations, if the figures are to enable reliable comparisons to be made. Among the necessary data he includes the fineness or cross-sectional area, but more particularly the length of thread between the clips, as in the case of shorter threads the figures are usually somewhat higher than for longer threads ; also the rate of increase of the load and the relative humidity of the air.

The Extensibility, that is, the elongation of the thread before breaking when determining the breaking load, is usually about 15 to 25 per cent of the length of thread and about equal to that of degummed natural silk, and is therefore about double the extensibility of cotton, but only about one-half that of wool.

In the table on the next page, a few results obtained by P. Krais in the Dresden Textile Research Institute (*loc. cit.*, page 12), are given.

It is remarkable that in the case of fine cuprammonium silk the elongation is increased more than two-fold in the wet condition, whereas in the other cases, even in those of cuprammonium silk, it is always stated to be considerably lower.

The reader is also referred to the publication of the same Research Institution entitled Versuche über die Zerreissfestigkeit von Fasern und Fäden insbesondere von solchen aus Kunstseide und Stapelfaser

(*Experiments on the Breaking Strain of Fibres and Threads, and Particularly of Artificial Silk and Staple Fibre*), *Neue Faserstoffe*, 1919 pages 121 and 265.

The statement by P. Krais in that publication is very interesting, that on treating artificial threads with organic liquids such as petroleum, which produce no swelling but rather a shrinking of the threads, an appreciable increase of the strength above the dry strength is produced. Heating the threads for one or more hours at temperatures from 110° to 115° C., also definitely increased the dry strength, but not the wet strength.

The determination of breaking load is probably best carried out by generally known forms of special apparatus

	Deniers	Breaking load gm.	Elongation per cent
Cuprammonium silk, dry	1·4	3·3	8·3
,, ,, wet	1·4	2·4	11·6
Viscose silk, dry	5·3	12·4	11·2
,, ,, wet	5·3	6·1	7·9
,, ,, dry	6·6	13·6	13·8
,, ,, wet	6·6	6·2	10·3
,, ,, dry	8·1	18·9	14·0
,, ,, wet	8·1	9·3	13·3
Nitrate silk, dry	3·0	7·4	8·1
,, ,, wet	3·0	5·2	7·2
,, ,, dry	5·9	11·4	15·0
,, ,, wet	5·9	6·0	10·1
,, ,, dry	8·2	22·7	20·3
,, ,, wet	8·2	12·9	15·3
,, ,, dry	10·2	18·8	19·0
,, ,, wet	10·2	12·6	12·2
Acetate silk (English), dry	5·0	7·9	27·5
,, ,, ,, wet	5·0	6·6	24·4

(serimeters) such as that which has been sold for many years by Louis Schopper, of Leipzig. Figs. 94 and 95 show two modern forms of such apparatus, the former being operated hydraulically and the latter by gravity. Apparatus is also constructed to be operated by hand. Those operated by gravity are to be preferred, as in their case the rate at which the pull is increased is very uniform, which is not the case with the apparatus operated by hand. The forms operated hydraulically or electrically are also quite satisfactory, but they are ordinarily used for strong threads or yarns only.

Optical Behaviour. Detailed investigations on this subject have been carried out, more particularly by A. Herzog, and are described fairly fully in his book already referred to, *Über*

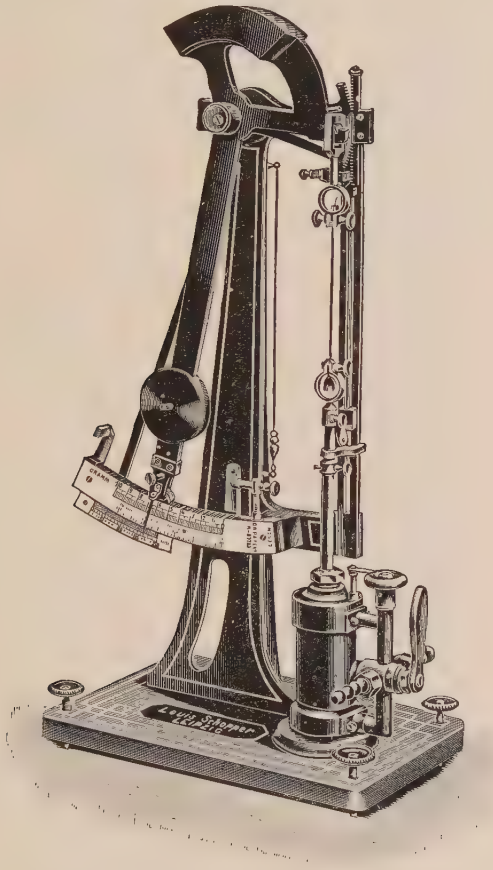


Fig. 94. Apparatus for Determination of Tensile Strength
Hydraulically actuated

die Unterscheidung der natürlichen und künstlichen Seiden, 1910, pages 40 and 77, andare illustrated by excellent micro-photographs.

We must refer the reader especially to this work, which describes the behaviour of artificial silks in polarized light, their

indices of refraction and their appearance under the ultra-microscope, as we can only describe here the general features of the optical behaviour of artificial silks, and can merely select certain specially interesting points arising out of Herzog's work.

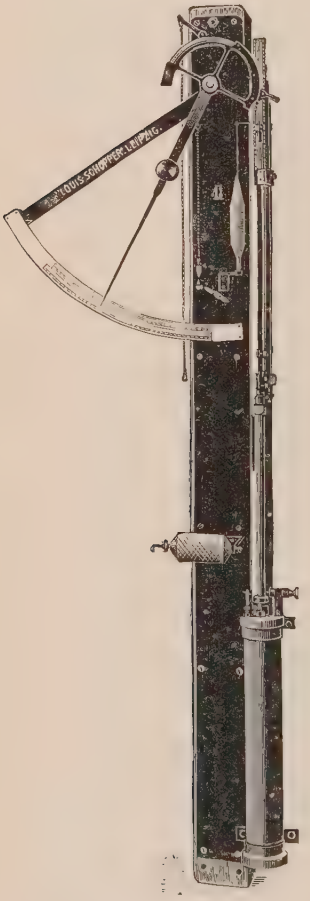


Fig. 95. Apparatus for Determination of Tensile Strength
Actuated by gravity

When testing in polarized light it is usually advisable to work with crossed nicols, with very weak double refraction and the help of a gypsum plate (Red No. 1).

All artificial silk fibres, and also the natural silk fibre, show double refraction. Collodium silk shows particularly beautiful coloured and luminous polarization effects, which vary greatly and are often arranged in more or less parallel lines. A similar effect is seen with viscose silk, but the colours are not so fine and parallel lines are less frequent. The appearance of cuprammonium silk is entirely different, as the fibre appears dull and is usually uniformly brownish-orange in colour and uniformly greyish-blue between parallel nicols. Natural silk is fairly uniformly bluish- or yellowish-white, and more rarely shows reddish-violet polarization colours. Acetate silk, when examined between crossed nicols, merely shows a very slight or even inappreciable increased luminosity of the field. Between parallel nicols with the help of a $\frac{3}{4}$ mica plate the fibre appears white at an angle of $+ 45°$ and brown at an angle of $- 45°$. When immersed in lemon oil it is almost invisible.

The two main indices of refraction for the sodium line

observed in a longitudinal view of the fibre, vary considerably for the various varieties of artificial silk, and are relatively very small for acetate silk. In the case of all silks, except acetate silk, the refraction along the axis is greater than in a direction vertical to the axis, corresponding to the different orientation of the ellipsoid of optical elasticity, the longer axis of which is at right angles to the longitudinal axis in the case of acetate silk, but parallel to the direction of the fibre for other silks ; whilst conversely the shorter axis is parallel to the direction of the fibre in the case of acetate silk, and at right-angles thereto in the case of other silks. This characteristic difference may be used for the rapid and certain identification of acetate silk.

The indices of refraction vary somewhat when determined parallel and vertically to the axis of the fibre. For the mean indices of refraction Herzog gives, for example, the following figures—

Natural silk, 1·567 ; cotton, 1·557 ; gelatin silk, 1·540 ; cuprammonium silk, 1·538 ; collodium silk, 1·531 ; acetate silk, 1·477.

Thus, the more technically important artificial silks do not vary seriously in their main indices of refraction.

Whilst natural silks show a splendidly-coloured parallel structure under the ultra-microscope, under which gelatin silk appears optically empty, the artificial silks show a more or less marked reticulated structure. This is certainly very weak in the case of acetate silk and collodium silk, but fairly strong in viscose silk and very conspicuous and luminous in cuprammonium silk.

Chemical Properties

These vary more or less according to the nature of the artificial silk. We have seen that cuprammonium silk and viscose silk show a very definite cellulose hydrate character. Collodium silk must also be considered to be mainly cellulose hydrate after denitration, although it still contains small quantities of nitrogen, to which various characteristic reactions of collodium silk are due. Acetate silk, on the other hand, is

an acetic ester of cellulose, which differs entirely in behaviour from cellulose hydrates. Similar remarks apply to cellulose ether silk. Those silks which are obtained from other chemical compounds, such as gelatin, casein, and so forth, naturally show an entirely different chemical behaviour.

The properties of cellulose and cellulose hydrate have already been described in the General Section (page 20 *et seq.*) ; those of the cellulose acetates and cellulose ethers have also been described (pages 316 and 325). Thus the fundamental chemical properties and differences of these silks have already been dealt with, and we may here confine ourselves to the following data, which refer rather to the finished silks than to their fundamental substances, and are worth mentioning as they furnish special analytical methods of distinguishing between them.

Water Contents. Those artificial silks which are cellulose silks are just as hygroscopic as natural silk. A detailed investigation, for example, by the Elberfeld Conditioning House led to an average moisture content of rather more than 11 per cent H_2O. The same figure is given by G. Laaser for staple fibre in *Deutsche Faserst. u. Spinnpfl.*, 1919, page 265. Exactly as in the case of natural silk, the commercial weight is assumed to be 11 per cent greater than the dry weight determined at 110° C.

Cellulose acetate silk shows other characteristics. The free hydroxyl groups, which are the main cause of hygroscopicity, are here esterified, and the affinity for water is therefore very small. For this reason the amount of moisture in acetate silk is about 3 per cent only.

G. Baroni (*Die Kunstseide*, 1925, page 59) found the highest absorption of water after dyeing in the case of collodium silk, much smaller figures for viscose silk, and the smallest values for Glanzstoff (cuprammonium) silk. It should be added that the differences between the two last-named silks are in many cases scarcely noticeable. Baroni believes, however, on the basis of the figures communicated by him, that the behaviour of the various varieties of artificial silk with regard to moisture is a useful help in distinguishing collodium, cuprammonium and viscose silks.

The absorption of water is accompanied by more or less marked swelling of the fibre. With the exception of

acetate silk, which is quite inactive in this respect, all artificial silks swell greatly in water, the general increase in diameter being more than 30 per cent of the diameter of the air-dried fibre, but usually exceeding 40 per cent and sometimes exceeding 60 per cent. It is thus considerably higher than in the case of natural silk, in which it amounts to 10 to 15 per cent only. These differences explain the great loss in strength which the artificial silks show in the moist condition, and by which they are distinguished from natural silk, as already explained.

With regard to the affinity for dyestuffs of the various artificial silks, see the section on the Dyeing of Artificial Silk, page 339.

The behaviour of artificial silks with various dyestuffs is sometimes used for distinguishing the various varieties. If, for example, samples of threads of the various kinds of artificial silk are immersed for a few minutes in very dilute Methylene Blue solution and then washed with water, until the liquid no longer shows a bluish colour when examined in a deep layer, and the sample dried, collodium silk shows a strong bluish-violet colour, whilst viscose silk is light blue, cuprammonium silk only faintly blue, and acetate silk quite colourless. Collodium silk and acetate silk can be distinguished from one another and from the two other varieties of silk with certainty. The difference between viscose silk and cuprammonium silk is sometimes so small that a reliable opinion cannot be formed and other reactions must be used.

According to F. Beltzer (*Moniteur Scientifique*, 1911, page 633) ruthenium red (ruthenium ammonium oxychloride) may be used in a similar manner for distinguishing the various varieties of artificial silk. This reagent does not colour cellulose nitrate ; it colours cellulose dinitrate strongly red, viscose silk intensively pink, cuprammonium silk barely reddish. P. Maschner (Lehne's *Färber Ztg.*, 1910, page 352), distinguishes the various varieties by the colours which are produced on submerging them in concentrated sulphuric acid. This reaction must, however, always be carried out comparatively, together with known samples of artificial silk. Collodium silk at first remains absolutely colourless, and a weak yellow colour of the liquid is only to be observed after $\frac{3}{4}$ to 1 hour. Cuprammonium silk at once assumes a weak yellowish or brownish colour, and after $\frac{3}{4}$ to 1 hour the liquid has acquired a brownish-yellow colour. Viscose silk at once shows a weak but definite reddish-brown coloration and the liquid is rust-brown in colour after $\frac{3}{4}$ to 1 hour.

All collodium silks give an intensive reaction for nitric acid with diphenylamine in concentrated sulphuric acid, namely, a dark-blue coloration.

There are a whole number of reactions which differentiate the artificial silks from natural silk. As a preliminary test, one may use an examination by hand of the strength in the wet state, which shows a great difference between natural and artificial silk. Natural silk, like wool, dissolves easily in dilute (about 8 per cent) caustic alkali solution and also in an alkaline copper and glycerin solution, whereas cotton and artificial silks do not dissolve, excepting gelatin silk or casein silk. If a sample of a mixed fabric is heated to 200° C. for about 10 minutes, the artificial silk threads are carbonized and are completely removed in the form of dust on rubbing. Wool, cotton and natural silk are unaffected by this treatment. By then comparing the remainder of the fabric with a sample of the untreated material the proportion of artificial silk, which is now missing, can be exactly determined. H. Manea (*L'Industrie textile*, 1910, page 370), distinguishes natural and artificial silk by dissolving the sample in concentrated sulphuric acid with the addition of a little oleic acid and water. In the presence of artificial silk only, a red to violet coloration is said to be obtained. According to Formhals (*Chem. Ztg.*, 1919 Vol. 43, page 386), a solution of natural silk in concentrated sulphuric acid is diluted with water and neutralized with sodium hydroxide solution until it is strongly alkaline, and diazotized p-nitraniline solution is then added. In the case of natural silk a red coloration is obtained, whilst with artificial silk a yellow coloration only occurs.

Regarding the physical and chemical examination of artificial silk we must refer to *Laboratoriumsbuch für die Kunstseide- und Ersatzfaserstoffindustrie*, by H. Jentgen (Halle, 1923).

CHAPTER XVI

APPLICATIONS AND USES OF ARTIFICIAL SILK

We will conclude the long journey which we have made from the cotton plantation and the woodland, the source of the raw material for artificial silk, which has led us, by way of a short description of wood-pulp manufacture and through all the departments of a modern artificial silk factory, and we will now devote a moment to the finished textiles, in order to obtain a general view of the various methods of applying artificial silk, and some information on the manner in which it is converted into textile fabrics.

Sizing, Finishing, and Weighting. Before the undyed or dyed artificial silk is converted into finished fabrics, more particularly on the weaving loom or knitting or embroidery frame, the thread must be prepared for this further treatment, exactly as in the case of other fibres, such as cotton and wool. In order to pass through the various machinery easily and without damage it must possess a certain elasticity and smoothness as otherwise, for example, the sharp edges of the comb of the weaving loom would tear many fibres which would accumulate in front of the reeds and cause the breakage of further threads. Moreover, the warps, which are exposed to considerable tension in the weaving loom, require to possess considerable elasticity.

It was found by experience that the dressing usually applied to cotton, wool, and so forth, namely, impregnation with smoothing substances, which render the fibre soft and elastic, could not be applied directly to artificial silk. More particularly, the sizing of the warps, that is, the treatment with a finish calculated to make them smooth, encountered considerable difficulties for a long period. The mixture formerly recommended was a gelatin solution containing 2 to 3 per cent of glycerine and 1 to 2 per cent of Monopol soap. (See *Leipz. Monatsschr. f. Textil-Ind.*, 1914, page 170.) A better result is

said to be attained with a solution of equal parts of glue and gelatine in about 12 times the quantity of water, which is boiled, and to which there are then added per kilogram of glue—200 gm. of olive oil, 50 gm. of soda, 200 gm. of Turkey-red oil and 100 gm. of potato starch which has been hydrolysed with diastaphor. The hanks of artificial silk are passed through the solution or suspended in it for a short time, and then centrifuged.

Finally, untwisted warp yarns were used for the warp instead of twisted warp threads, and these proved advantageous after suitable means of sizing them had been discovered. For example, A. Lauffs recommends the following procedure in German patent 365,668 : To 100 kg. of artificial silk of 120 deniers a bath is used, not exceeding 1,700 litres, containing 5 kg. of glue, 1 kg. of soluble starch, and 2·5 kg. of Marseilles soap. Sizing is to be carried out at 50° C. The material is not to be used immediately, but to be left, with frequent turning, until the quantity of sizing material in the drained or pressed liquid no longer diminishes, and the threads therefore no longer absorb further sizing material from the solution. In German patent 417,924, H. Baumann recommends a finish for the same purpose consisting of the well-known mixture of soap, coco-nut or palm kernel oil, mineral oil and fire-proofing salts already used for the impregnation of sewing cotton. (See H. Walter, *Zts. f. d. ges. Textilindustrie*, 1924, page 561.) According to German patent 348,194, J. Korselt increases the strength and elasticity of artificial silk and other fibres by treatment with ferments.

The sizing is usually washed out of the finished textile fabric, and this is particularly necessary if the goods are to be dyed. If a hard and highly resistant fabric is desired, which requires no further dyeing, it may be desirable not to wash away the size but to treat it with chemicals which harden the glue and render it resistant to water, such as formaldehyde, potassium bichromate and so forth. In order to remove the size from acetate silk or remove the size and de-gum mixed fabrics of crude natural silk and acetate silk, Soc. pour la Fabrication de la Soie " Rhodiaséta " proposes the use of soap baths with the addition of neutral potash salts, in German patent 395,829.

For mixed fabrics of wool and artificial silk or of half wool and artificial silk, wet dressing is carried out according to the same principles as for pure woollen fabrics, allowing for the special properties of artificial silk by avoiding all friction, too strong a tension on the fabric, and so forth. The material is singed, washed, steamed, and so forth in the manner usual for woollen goods. Steaming is only used for smooth goods, whereas for rough goods, such as friezes and so forth, it is usually omitted. The fabric is bleached with hydrogen peroxide or sodium peroxide, and then, after souring and rinsing, it is treated with sulphurous acid, again well rinsed, and then dyed, if it has not already been dyed in the yarn. According to the character of the fabric, it is then finished with starch or with size and finally dried. The usual warping, steaming, and pressing operations then follow.

Mixed fabrics of cotton and artificial silk are often dyed directly after singeing in the case of light fabrics or of dark shades. Stronger and heavier fabrics and light coloured goods are first cleaned. The cleaning usually consists of treatment with diastaphor for removing the size, followed by boiling with soda and soap. Dark goods are then dyed, sometimes after steaming for a short time. Light-coloured goods are first bleached, usually with bleaching powder or sodium hypochlorite (electrolytic bleach) and are then treated with antichlor and rinsed. White goods are usually also blued. The fabric is then dried, usually on the tentering machine, trimmed, and finally finished in the usual manner with a mixture of starch and salt, and the process completed by calendering, and so forth. Coloured goods are, of course, dyed before they are finished.

It is impossible to weight artificial silk in the manner adopted for natural silk, in which the weighting often amounts to several hundred per cent of the fibre. In so far as proposals for this purpose exist they are confined to weighting up to 3 to 5 per cent or rarely up to 6 to 10 per cent. As an example of a preparation proposed for this purpose, we may mention a solution of 12 gm. magnesium sulphate and 6 litres of Turkey-red oil in 100 litres of water, which is warmed to 35° C., and

250 gm. of gelatin then added, which is said to be well suited to the purpose. (See *Zts. f.d. ges. Textilindustrie*, 1914, page 368.) In German patent 338,653 the Auergesellschaft describe a process according to which the hydroxides of heavy metals are fixed on the artificial silk fibre, more particularly for the purpose of manufacturing gas mantles, by means of gases of alkaline reaction (ammonia) which may be diluted by inert gases. According to patent of addition 411,265, lanthanum salts and kindred compounds are to be used in the same manner.

A great many patents deal with attempts to produce a fibre from artificial silk which shall resemble wool as closely as possible. (See the section on "Staple Fibre," page 391.) Attempts were made to solve this problem partly by mechanical treatment and partly by chemical methods. E. Schülke, for example, in German patent 342,223, describes a process according to which weakly twisted and dried artificial silk threads are roughened by breaking individual outer fibres and then finally twisted. The roughening is to be achieved, for example, by passing the threads between two rollers, one of which is retarded and is coated with emery-cloth. According to German patent 406,506 of the Paverin A.-G., fibres are satisfactorily crimped by first gelatinizing them in suitable reagents, such as caustic alkali solution, zinc chloride, or a sulpho-cyanide solution, then shrunk by a coagulating agent and finally dried without tension. According to R. Clavel's German patent 411,798 woollen effects with a soft feel can be obtained, particularly in the case of acetate silk, by treatment with organic acids under definite conditions.

ARTIFICIAL SILK FABRICS

We will now give a short description of the more important textiles manufactured from artificial silk.

Trimmings, Embroidery, etc. About twenty years ago, when the properties of the artificial silk thread were unsuited for its widely extended use, and particularly for weaving purposes, a demand could only be created on account of its exceptional lustre. It was therefore chiefly used at first for goods in which lustre played an important part, such as various kinds of

trimmings, braidings, tassels, ribbons, and so forth, which were used for decorating clothes and hats, and for similar purposes. Belts, complete hats, and so forth, were also manufactured of artificial silk braid.

For the manufacture of such articles, artificial silk is usually employed of a quality of 120 to 180 deniers. The threads as received from the dressing or dyeing establishment are first re-wound from reels on to small wooden bobbins, as used in many spinning machines, and, for example, directly on to the bobbins of the braiding machine, in case the silk is simply to be wound and not doubled. This is, however, seldom the case ; for example, for the manufacture of "*lace à la reine*," which is used for embroidery thread or ruches, and so forth. Usually, 2 to 6 threads are doubled on the doubling machine, and the compound threads so obtained are plaited on the plaiting machine to a narrow braid. Braids are produced in such a manner that they show the same pattern on both sides and the warp is nowhere plainly visible. This can, of course, be effected in various ways so that the braids are of various patterns, according to which they are described as "single strand," "double strand" and "triple strand" braids, which latter is known by the name of "Hercules" braid. The working of artificial silk on the braiding machine is entirely satisfactory, and some maintain that artificial silk can be used more easily than cotton. The thread runs well and lies very smoothly, and it is said that such excellent results cannot be achieved with cotton.

Artificial silk is similarly used for products similar to braids, such as laces, edgings, borders, furniture trimmings, carriage and livery trimmings, part of which are produced on the braiding loom and part on the trimming loom or ordinary ribbon loom.

Other trimmings manufactured from artificial silk include laces, braids, fringes, tassels, rosettes, purls, pom-poms, covered buttons, and so forth, in fact all woven materials used as trimmings. Various properties of artificial silk are especially useful for these. Thus, it is preferred to real silk, for instance, for fringes and tassels, on account of its greater stiffness.

Laces. These can be manufactured of artificial silk both on the hand machine and the power machine, and are largely used for women's wear. Viscose or collodium silk is also much used for guipure laces, produced by the selective carbonizing process, as it has the advantages over natural silk of a higher lustre and lower price. The artificial silk used for this purpose must, of course, be particularly resistant to carbonizing, that

is, it must resist the temperature of the carbonizing oven, which is usually 120° C., and its colour must not be changed at this temperature. For this purpose artificial silk dyed with substantive colours is, therefore, preferred, which has not been treated with sulphuric acid.

Guipure laces are, as is well known, embroidered on a base which is usually constructed of cotton fabric which has been impregnated with acid salts or with salts which liberate acid at high temperatures, such as magnesium chloride, bisulphate, and so forth. When the completed fabric is heated in a carbonizing oven the base is destroyed by the action of the salts with considerable charring, and is disintegrated so that it is readily removed by beating, and the lace alone remains. The goods must be kept very dry before carbonizing so that no salt may diffuse into the artificial silk, as this would then also be destroyed. (See H. Stadlinger, *Kunststoffe*, 1912, page 281.)

Woven Fabrics. Ordinary artificial silk ribbons form an intermediate stage leading to broad fabrics, and are produced on the ribbon loom or on the bar-loom in all widths, from about 2 mm. to 25 cm. with a twill, satin or calico weave; they often contain cotton, forming half-silk ribbons and so forth.

Originally, various fabrics were produced in which artificial silk formed the weft only, but it is now used without difficulty either doubled or not, for warp threads, and pure artificial silk fabrics are produced in which both the warp and the weft consist of artificial silk, although such materials even now occasionally leave something to be desired. Thus, the limited elasticity of the artificial silk fibre, compared with real silk, entails special care if the former is used for warp threads. Fibres of medium counts of about 150 deriers are preferably used for weaving, though lower counts of 80 to 90 deniers are also used for warps. Simple untwisted weft silk is now often used for the warp, and a special finish for this purpose has also been referred to.

The extent to which endeavours were directed to the use of artificial thread as a warp are indicated by the remarkable and certainly somewhat expensive expedient proposed in British patent 10,186/1910 of Wilkinson and the Bradford Dyers' Association, which consisted in using a warp spun from

artificial silk and wool (or silk), followed by the removal of the animal fibre with caustic alkali solution after the fabric had been woven.

The lustre and fine colour effects of artificial silk are particularly useful for the manufacture of tie materials, and such materials were among the first products of artificial silk weaving.

Artificial silk then found more extended application together with cotton, wool, or silk, either as fancy threads or as weft threads. Half-silk linings belong to this class, and are produced both with a cotton warp and artificial silk weft, and with an artificial silk warp and a cotton weft. When artificial silk is used for the warp the weaving must be carried out on special silk-weaving looms. So-called washing silk materials of artificial silk are increasingly used for women's clothes, blouses, and so forth. " Washing silk " of artificial silk is a half-silk material with a tabby or linen weave, a cotton warp and artificial silk weft, for which specially suitable artificial silks are used. Artificial silk is woven together with cotton or silk for light summer fabrics, blouse materials, and so forth. Silk taffetas are frequently produced with a real silk warp and an artificial silk weft, and the so-called *mousseline de soie* is similarly produced. Many silk fabrics are also produced with artificial silk threads as either weft or warp, and real silk or wool. Worsted cloths, and so forth, are also produced with artificial silk as an excellent fancy thread in blended designs, and so forth. Cloths are now produced in large quantities consisting of so-called " mixed fabrics " of wool and artificial silk, and also of cotton and artificial silk, or of threads of all three kinds. Materials which possess the lustre of artificial silk are frequently obtained by weaving artificial silk, together with cotton, mercerized in hank form. According to German patent 398,583, of W. Marshall, it is possible, when using acetate silk, subsequently to mercerize the fabric containing unmercerized or incompletely mercerized cotton and cellulose acetate, as a strong mercerizing solution containing 21 to 27 per cent of sodium hydroxide does not appreciably attack cellulose acetate at temperatures below 15° C. during a short period. A similar process is described in German patent 412,164, of Courtaulds, Ltd., according to

which the artificial silk is dressed, for example, with gelatin, before mercerizing.

Hosiery. Women's stockings, knitted underwear and jumpers and so forth, of pure artificial silk, are at present very fashionable, and enormous quantities of artificial silk are at present used for these articles, accounting for 50 per cent of the total artificial silk consumption in England and 60 per cent of that in the United States. Rather heavy artificial silk yarns of about 300 deniers are generally used for these articles. Knitted ties, shawls, waistcoat slips, fabric gloves and so forth, are produced wholly or partly of artificial silk in considerable quantities.

Embroidery. Artificial silk is used both for hand and machine embroidery, partly in the form of untwisted open threads and partly as doubled threads.

Furniture Fabrics. Artificial silk has been used for a considerable time for the manufacture of decorative furniture fabrics, plushes, curtains, hangings, wall coverings, carpets, and so forth, more particularly owing to the highly lustrous effects, which were not otherwise obtainable. It is also said that it is much easier to remove adherent dust from such materials when they consist of artificial silk.

For Leather and Fancy Goods and allied industries, artificial silk is increasingly used for the linings of satchels and other leather goods, as linings for cardboard boxes, and so forth. (See R. Schreiter, *Kunststoffe*, 1914, page 336.)

Technical Applications. The application of artificial silk for technical purposes is very considerable. The most various fabrics, filter cloths, sieve cloths, bolting cloths, belts, and so forth, are manufactured from artificial silk or from mixed fabrics containing the same. Artificial silk is frequently used in the form of collodium silk, which has not been denitrated, in the munition and pyrotechnic industries, for the manufacture of fuses, cartridge cases, and so forth.

Artificial silk threads have also proved very useful for the manufacture of gas mantles, and the gas-mantle industry has become one of the largest consumers of this product. (See *Kunststoffe*, 1912, page 193, and 1913, pages 20 and 260.)

In the electrical industry artificial silk appears to be gaining ground as an insulating material for wires, and so forth. The first attempts, which were made about twenty years ago, led to the discovery of too many disadvantages of artificial silk compared with natural silk. Its insulating power was lower, the required thickness was greater, the specific gravity higher, and more particularly the price was higher ; but now these disadvantages have partly disappeared and, more particularly, the price is considerably lower than that of natural silk.

Artificial Hair. Finally, we may mention the manufacture of wigs and transformations of artificial silk, the stronger counts of which furnish an excellent and cheap hair. The gloss of threads for this purpose is naturally removed. Details of this process will be mentioned in connection with the similar application of artificial horsehair (see pages 382–383). (See also *Kunststoffe*, 1914, pages 361 and 374.)

Artificial Silk Waste. This finds many applications. The better qualities of relatively long-stapled waste are spun either alone or with cotton, wool, ramie fibre, and so forth, to produce threads for weaving. Details will be found on page 389.

Other forms of waste are used for the manufacture of cheap trimmings, such as fringes, purls, button covers, and so forth, and also for felt manufacture. On the other hand, attempts to use this waste for the production of special effects in the manufacture of paper have not so far been very successful. (See also A. Dulitz, *Kunststoffe*, 1911, page 107.)

CHAPTER XVII

VARIOUS OTHER FORMS OF ARTIFICIAL THREAD

In the preceding sections we have concluded our description of the manufacture and properties of artificial silk and its uses.

These fine and multi-fibred products are not, however, the only products of the artificial silk industry. From the commencement of the industry various other forms of artificial thread have been produced by it, apart from artificial silk, and we will now consider these separately.

As the form of the nozzle aperture is the main factor in producing the cross-section of the thread, it is obvious that by altering its cross-section threads of the most various kinds can be produced. If, for example, instead of the multiple nozzles with numerous fine openings, such as are used for artificial silk production, a single nozzle of relatively wide aperture is used, a thread is obtained of about the thickness, or of greater thickness, than an artificial silk thread, which does not, however, consist of several individual fibres but of a single homogeneous thread (monofil) of relatively large cross-section. The spinning aperture of such a monofil nozzle need not necessarily have a circular cross-section, but may take the form of a long slit, in which case a thread is produced which constitutes a more or less wide ribbon, and by special arrangements the form of the thread can be varied in many other directions.

In other respects, the method of producing such threads and the necessary machinery for the purpose does not differ much in principle from that used for ordinary artificial silk, excepting for threads of special character, such as those which include a natural fibre.

We have already mentioned in the Historical Section that the manufacture of various forms of artificial thread of this kind was always an economically important branch of the artificial silk industry, and we may remind the reader of the first artificial threads constructed by Swan, Wynne and Powell,

for the manufacture of electric lamp filaments, consisting of such single threads resembling horsehair.

ARTIFICIAL HORSEHAIR. (MONOFIL)

Horsehair substitutes were formerly marketed by most artificial silk works under various special names, such as "Viscellin" yarn, with a cotton core; acetate horsehair; "Helios" (viscose monofil); and "Pan," by the Fürst Guido Donnersmarckschen Kunstseiden- und Acetatwerken; "Sirius" by the Vereinigten Glanzstoffabriken, Elberfeld; "Meteor" (from cellulose nitrate), and "artificial hemp" (consisting of several adherent individual filaments), by the Ver. Kunstseidefabriken, Kelsterbach; "Crinol-star" by the Viscoseseide-Fabrik, Emmenbrücke, and so forth.

A special form of manufacture of artificial horsehair has already been mentioned by way of example; a single, wide nozzle aperture of circular cross-section is used, from which the spinning solution issues in a relatively thick stream, which is coagulated in a suitable bath and further treated in hank form as a single thread. This is the simplest, most obvious and most usual method of production of artificial horsehair and similar materials.

The Vereinigten Glanzstoffabriken, Elberfeld, spin artificial horsehair from cuprammonium solution by precipitation with concentrated caustic alkali solution, and treat the filaments, before washing, with a further quantity of similar caustic alkali solution, which may contain as much as 6 per cent of ammonia, according to British patents 1284/1905 and 1745/1905, German patents 186,766 and 188,113, Austrian patents 32,377 and 33,272, French patents 351,206 and 351,207, and U.S. patents 804, 191 and 856,857. The process of the patents already referred to on page 248 of the Vereinigten Glanzstoffabriken, Elberfeld, according to which the threads precipitated from cuprammonium cellulose solutions by sulphuric acid are led on to a roller revolving in concentrated caustic soda solution, is excellently suited for the manufacture of such single threads according to the patent specification. According to French patent 392,868, A. Lecoeur produces artificial horsehair threads from cuprammonium cellulose solutions by the use of an alkaline spinning bath, which consists of equal parts of 20 to 25 per cent sodium carbonate solution and 25 to 30 per cent sodium hydroxide solution. The threads are wound on to a roller which revolves in a bath containing concentrated sodium carbonate solution to which 7 to 8 per cent of sodium hydroxide solution is added. The copper is then removed in a bath of sodium bisulphate containing about 4 per cent of free acid.

E. Crumière dips the threads, obtained from cuprammonium solution by precipitation with dilute acetic or sulphuric acid, for a short time in a warm concentrated solution of zinc chloride of sp. gr. 1·7, then washes with acidified water; then with pure water, and dries (British patent 6766/1908 and French patent 377,118); or he spins the cuprammonium cellulose solution directly into zinc chloride solution to which sodium or potassium hydroxide has been added. A sufficient excess of alkali hydroxide must obviously be added to retain the zinc in solution as alkali zincate (British patent 7126/1908, French patent of addition 9067 to patent 377,118, and U.S. patent 911,868). The manufacture of artificial horsehair by the dry spinning process is proposed by Diamanti and Champion in French patent 377,494. Regarding the production of artificial horsehair from solutions of cellulose or of pretreated cellulose, in acids, see B. Borzykowsky, French patent 424,428, Swiss patent 56,107, and U.S. patent 1,010,222. Attempts have also been made to produce artificial horsehair from gelatin solution. Ordinarily, relatively dilute warm aqueous solutions were used, and the extruded threads were carried on belt conveyors for a considerable distance to the winding contrivance. The product which was obtained was as unsatisfactory as gelatin silk. According to German patent 183,001 of L. E. Jannin, better threads are obtained from concentrated gelatin solution. He uses, for example, a solution of 1 kg. of gelatin and 100 grm. of glycerine in 1 litre of water, and maintains the thread under tension for some time in a special apparatus before winding, so that it may be uniformly dried without shrinking and sticking; but even by this process no satisfactory results were obtained.

The above method of producing artificial horsehair by a process quite similar to the artificial silk spinning process was not the only one which was used technically, although it was the simplest. The reason why other methods were sought for, although these were usually more complicated, was the difficulty of coagulating such thick threads. It is obvious that the conditions for the precipitation and fixation of a thin individual fibre of ordinary artificial silk are entirely different from those necessary for a fibre 20 or more times as thick. The conditions of the spinning process, more particularly the composition of the spinning bath, the speed of output of the thread, and so forth, as used for ordinary artificial silk could not, therefore, be immediately applied to artificial horsehair. In that case brittle and perfectly dull threads were often obtained, which possessed no tenacity and which could not be knotted, as the thread always broke when the knot was tightened.

A method which was tried in order to overcome these difficulties was to ensure conditions more similar to those of the production of ordinary

artificial silk by using nozzles with two or more apertures, thus producing two or more individual fibres which were thicker than the ordinary constituent fibres of artificial silk but still appreciably thinner than the artificial horsehair threads. These individual fibres were allowed to join immediately after their production, at such a short interval after their extrusion from the spinning apertures that they were still able to cohere to a single homogeneous thread. (See British patent 20,461/1900, German patent 125,309, Austrian patent 5195 and U.S. patent 680,719 of the Vereinigten Kunstseidefabrik A.-G., Frankfurt a. M.) Another process proposed by the same firm, which was quite similar in principle, was to pass threads of cellulose, or cellulose derivatives, such as cotton, ramie, nitro-cellulose, artificial silk of any kind, and so forth, through a suitable solvent in such a manner that the threads superficially gelatinized until they were almost dissolved and could then be united to a single, coherent artificial horse-hair thread. For example, cellulose threads (artificial silk) were passed for this purpose through a cuprammonium or zinc chloride solution, or nitro-cellulose threads through a solution of ether-alcohol. Any faulty portions of the thread were improved by subsequent treatment with a solution of gum, gelatin, or collodium. (See British patent 17,759/1900, German patent 129,420, Austrian patent 8359, and U.S. patent 713,999.) A similar process was described in British patent 10,487/1897 of Dreaper and Tompkins. In order to enable the process to be carried out with twisted artificial threads, the twist was removed before the treatment by twisting in the opposite direction (German patent 181,784).

The threads produced by the above-mentioned processes were essentially more or less homogeneous agglomerates of uniform material. Another method of producing artificial horsehair, which could also be carried out fairly simply, consisted in applying a homogeneous, thin, lustrous coating of artificial silk material to a thread of natural fibre, such as cotton, linen, or silk, so that an artificial horsehair was produced consisting of a core of natural fibre with an artificial silk coating. This process was carried out, for example, by first passing the thread of natural fibre, forming the core, through a solution of collodium, viscose, cuprammonium-cellulose or cellulose-acetate solution and then through a suitable precipitating bath, and finally washing, bleaching, and dyeing, as in the case of artificial silk.

According to the process of the Fürst Guido Donnersmarckschen Kunstseiden- und Acetatwerke, for example, as described in British patent 23,683/1906, German patent 189,140, Austrian patent 29,999, and French patent 370,741, the original threads were passed through viscose solution, then carried vertically upwards with the adherent solution through adjustable openings and then through a coagulating

bath in the usual manner. The product was marketed as " Viscellin " yarn. Schaumann and Larsson (French patent 333,246) proceeded in a similar manner, using collodium. The process of C. N. Waite (U.S. patents 791,385 and 791,386) was similar in principle, although it differed in details. He passed threads of suitable thickness through a viscose solution, allowed the adherent solution to dry, and repeated this operation until the threads acquired the desired thickness or weight. They were then softened in water and fixed and treated further in the usual manner. E. M. S. Galibert produces a thread of peculiar structure by passing the core thread with the adherent cellulose solution through a spinning nozzle, the bore of which is only slightly greater than the diameter of the thread, and choosing the other conditions in such a manner that the thread is not uniformly coated with an adherent layer of the spinning solution, but on the contrary, a new thread adheres to the core thread in spiral windings, the pitch of which varies according to the rate of withdrawal (French patent 442,117). The gelatin silk process has already been used in a similar manner for coating natural fibres, for example, of silk or cotton, as described, for example, in Swiss patent 20,433 of M. Bruggisser & Co.

Elberfelder Farbenfabriken describe in German patent 227,238 a nozzle consisting of a tapered tube of elastic material for coating threads with cellulose acetate. Regarding similar nozzles for the production of composite threads, see German patent 252,059 of B. Loewe, and French patent 421,900 of Soc. Française de la Viscose.

Various proposals have been made to prepare the core threads by a special treatment before passing them through the cellulose solution. Impregnation with sizing preparations has not been found suitable for the purpose, as it thickens the core thread too much. According to German patent 7275, the core thread was denitrated and then deoxidized, but this was found to take too much time and trouble. A relatively simple process was proposed by Maschinenbauanstalt Humboldt in German patent 413,818. It consists in parchmentizing the core thread by sulphuric acid, zinc chloride solution or similar materials before applying the layer of artificial silk.

The artificial horsehair products obtained by one or the other of the above described processes consist of cylindrical, lustrous threads of a diameter varying from 0·1 to 0·4 mm. As the cross-section is seldom exactly circular, the widest diameter does not absolutely determine the area of the cross-section, which is about 0·15 to 0·1 sq. mm., or about 100 to 1000 times the cross-section of most natural fibres, such as cotton, flax, or hemp.

Although the above-described processes did not all produce satisfactory products, qualities were marketed by the various firms which could hardly be distinguished in appearance, feel, and behaviour from natural horsehair without close examination.

They showed, however, one essential difference from natural hair, in so far as their length was unlimited, a feature which was of great advantage for their application. (See below.)

Chemically, the behaviour of artificial horsehair is, of course, closely similar to that of the corresponding artificial silk. With the exception of acetate horsehair, which is very resistant to water in common with acetate silk, the threads swell greatly in water, causing an increase in thickness of 30 to 60 per cent on the average.

The breaking load, which naturally depends not only on the cross-section but also on the nature of the substance of the thread, varies greatly for the different products. The specific breaking load, that is, the absolute strength per sq. mm. of cross-section, was found by A. Herzog to vary from 10 to 25 kg. (*Kunststoffe*, 1911, page 181). Herzog established the fact that in general finer threads showed a higher specific breaking load, that is, were relatively stronger, than thicker threads. This may be due, as already explained, to the more favourable conditions of coagulation of finer threads. Also, the strength of a thread containing a core of natural fibre is naturally relatively considerably higher than that of a simple thread containing artificial silk material only.

In the wet condition the strength of artificial horsehair is greatly reduced, as is that of artificial silk. This reduction in strength is naturally lowest in the case of acetate horsehair, which swells but little, but even in this case amounts to 15 to 30 per cent. In the case of the other artificial horsehairs from cellulose nitrate, viscose, and so forth, the reduction in strength when wet varies from 40 to 80 per cent.

According to A. Herzog (*loc. cit.*) the breaking load, M, of the moist thread can be calculated, allowing for gelatinization, in terms of the breaking load f of the moist thread expressed in grams, of the cross-sectional area s in the dry condition in millimetres, and the elongation q expressed in percentages. The equation is—

$$M = \frac{f}{S\left(1 + \frac{q}{100}\right) \cdot 1000} \text{ Kg.}$$

In the case of cellulose-acetate horsehair, Herzog found values M of from 8·0 to 13·1 kg., and for " Viscellin " thread, with a core, of 6·7 to 9·0 kg. ; whilst with the other products which he tried the value varied from 1·8 to 4 kg.

As might be expected, the elongation on breaking is very small in the case of threads with a core of non-extensible material, but is large for the other threads and usually increases considerably in the wet state. A. Herzog found the elongation on breaking, expressed in percentages of the original length, to be 5 to 6 per cent in the case of " Viscellin," 2 per cent for artificial hemp, and 25 to 30 per cent for cellulose-acetate horsehair, " Helios " thread and " Sirius " thread. The increase in elongation on rupture in the wet condition was found by him to be 20 to 30 per cent for cellulose-acetate horsehair and 46·7 per cent for " Sirius " thread.

Compared with natural horsehair, the far lower elasticity of the artificial product is a disadvantage which is, however, to some extent compensated by certain advantages, such as the unlimited length, good dyeing properties, and so forth.

The optical behaviour of artificial horsehairs is much the same as that of the artificial silks (see A. Herzog, *loc cit.*, page 182) ; more particularly cellulose-acetate horsehair coincides entirely with acetate silk in its behaviour in the polarization microscope, and in that way contrasts with all other artificial horsehairs and silks. As already mentioned, the arrangement of the optical elasticity ellipse in acetyl-cellulose products is, according to Herzog, such that the long axis is vertical to the length of the thread and the shorter axis parallel to the same, whereas in the case of other threads the reverse is the case.

The dyeing properties of artificial horsehairs correspond exactly with those of the corresponding artificial silks.

As already mentioned, the unlimited length of artificial horsehair constitutes a great advantage in its use. It enables the product to be used directly for weaving and plaiting braids, laces, and so forth, which can be produced on the ordinary braid-plaiting machine. Lustrous coloured artificial horsehair is mainly used for women's hats, hat bands, ribbons, trimmings, tassels, belts, cushions, and so forth. The de-lustred hair is used

for wigs, hair fabrics, brushes, and also for upholstery. (See *Kunststoffe*, 1914, pages 337 and 374.)

RIBBON-LIKE PRODUCTS, ARTIFICIAL STRAW, ARTIFICIAL HEMP, ETC.

These products, which are marketed by various firms, both white and in many colours, are among the most wonderful products of the artificial silk industry, on account of their lustre and the beauty of their colouring.

In order to produce a single thread in the form of a more or less wide ribbon, one could proceed in a manner similar to that used for the production of artificial horsehair, that is, by giving the nozzle aperture the shape of a long slit. The further treatment was then the same as in the case of artificial horsehair. Other methods have, however, also been tried, apart from simple spinning of the above character.

Thus, in British patent 7520/1906, German patent 184,510, Austrian patent 33,840, French patent 363,782, and U.S. patent 853,093, Vereinigten Kunstseidefabriken, Kelsterbach and F. Lehner describe a process for the manufacture of "artificial hemp-bast," consisting in causing threads of artificial silk or mercerized cotton or the like to cohere in the form of a band, a covering material such as chalk, zinc-white, heavy spar, sulphur, or the like, being added to the adhesive in order to remove the lustre of the product. It was found that viscose could advantageously be used as an adhesive, the threads being drawn through this material, which was subsequently coagulated and fixed by treatment with mineral acids. If the conditions of the coagulation were so adjusted that much sulphur was precipitated, the lustre could thus be removed, so that no other covering medium was necessary. According to Swiss patent 72,044 of C. Mann, the artificial straw obtained from cellulose threads can easily be deprived of lustre by dyeing in a soap solution with the addition of tanning materials, particularly if the product is impregnated with Turkey-red oil and dried before dyeing. According to German patent 365,451, J. C. Hartogs ensures that similar artificial straw, ribbons, and similar flat threads shall lie perfectly flat on winding, by placing a rod, such as a glass rod, close to the winding spool so that the fibre glides over the rod in flattened form.

According to French patents 436,186 and 436,187, J. E. Brandenberger first produces a broad, film-like band by direct precipitation and fixation of cellulose solution or by coating fabrics with such a solution and then fixing it, and cuts this band or fabric into fine strips of the desired width. (Regarding cut threads, see also page 393.)

Hollow Threads. Natural straw, which is, of course, not a flat band but a tube-like structure, could be replaced for many purposes—for example, in hats—by flat artificial cellulose bands, which were, therefore, frequently described as "artificial straw." Attempts were, however, made later to approximate more closely to the structure of the natural product by the production of hollow threads, in the form of tube-like structures of various forms and cross sections. It was to be expected that such a structure would show a different character, a different degree of softness and flexibility and another feel, and would be more suitable than the simple band-like thread for many purposes.

Such hollow threads could be produced in various ways. One could, for example, imitate the process used for the manufacture of rubber tubing, that is, the product could be produced immediately in the form of a continuous tube by a suitable nozzle aperture, or a hollow thread could be produced by cohesion of a spirally-rolled band. Finally, bubbles of air or other gas could be continuously produced in the thread, such bubbles either remaining separate from one another or actually uniting to form a continuous cavity within the thread.

The first above-mentioned method was the safest and most reliable, though not always the easiest, and it produced the best products. In this case the important point was to ensure that the tube-like structure should be equally coagulated within and without during production. It was, therefore, not sufficient simply to pass these products through a precipitation and fixation bath during spinning, as in the case of artificial silk or artificial horsehair, as in that case the outer layer only would be coagulated and fixed with sufficient rapidity.

According to French patent 430,939, P. Girard attempted to solve this problem by expelling the spinning solution under pressure through an opening in the middle of which an electrically-heated pin was situated. The solution emerged from the nozzle round this pin, and coagulation of the tube was effected by the warmth of this pin, both without and more particularly within. The external coagulation was completed by a spinning bath through which the hollow thread could be passed. This process did not, apparently, prove satisfactory in practice. It appeared simpler to coagulate the thread by the same spinning bath both within and without. For this purpose arrangement

were used in which the spinning solution was expelled through an annular opening whilst a concentric thin-walled tube within the annular nozzle aperture served to introduce the precipitating bath into the inner portion of the thread. The mouthpiece with the annular aperture was situated in a vessel filled with the spinning bath, so that the bath liquid bathed the outer surface of the hollow thread. (See, for example, British patent 17,495/1914 of Courtaulds, Ltd., and Wilson.)

Composite threads could also be produced by introducing another thread within the tubular thread, the former being either produced by the same spinning bath, or it could if desired be already twisted, dyed, and so forth. In order to avoid adhesion of the hollow thread to the core, when producing such hollow threads containing one or more cores, J. C. Hartogs arranged the apparatus described in German patent 247,418 in such a manner that both the inner and outer walls of the hollow thread and the cores were bathed in the precipitating liquid.

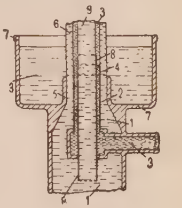


Fig. 96. Hartogs' Apparatus for Spinning Hollow Threads

Fig. 96 shows the arrangement in section. The spinning solution 1 is expelled through the annular aperture 2, whilst the precipitation bath 3 is passed through the thin-walled tube 4 concentrically arranged in the annular opening; this tube 4 may terminate either at the same or at a different level to the outer wall 5 of the annular aperture. The outer wall 6 of the hollow thread which is produced, is surrounded and coagulated by the precipitating bath in the vessel 7. Concentrically within the thin-walled tube 4 a second tube 8 is so arranged that a small annular space exists between the two, through which the inner precipitation bath flows. That portion of the spinning solution 1 which is destined to produce the core 9 of the thread flows through the inner space of the tube 8. In this manner a hollow thread 6 is formed, the outer surface of which is coagulated by the precipitation bath 3 in the container 7 and the inner surface by the precipitation bath expelled through the tube 4; whilst the outer surface of the core 9 formed by the tube 8 is also coagulated by the precipitation bath 3 passing out between tubes 4 and 8. The core is thus left loose in the hollow thread. A similar arrangement of the apparatus suffices for the production of hollow threads with several cores, the single inner tube 8 being replaced by a correspondingly larger number of tubes within the tube 4.

In these and similar arrangements the precipitation bath introduced within the tube-like structure is carried away with the tube and must be removed or replaced by water by diffusion during washing, the water being finally removed by drying. This filling of the inner space by the precipitation bath was a disadvantage which led to difficulties during the further treatment of the threads. L. Mönkemeyer, of Oberbruch, therefore devised an ingenious arrangement by means of which the inner precipitation bath only acted on the wall of the tube through a short distance and was driven backwards—that is, in a contrary direction to the path of the coagulated tube—during winding, and escaped

through an outlet port of the spinning nozzle. (See German patent 367,972 of the Vereinigten Glanzstoffabriken.)

Fig. 97 represents a section of this contrivance. The spinning solution is introduced at 7 into the annular space of the spinning tube 2, which it leaves through the annular nozzle aperture 1, from which it passes into the precipitating bath in the container 5, which can, of course, only act on the hollow thread from without. In order to coagulate the inner wall of the thread, the precipitation bath is introduced into the spinning apparatus at 9, passes through 6 into the inside of the tubular structure and fills this as far as the winding contrivance. The precipitation bath, which is driven backwards, escapes through the annular space 10 and the side tube 8 of the spinning apparatus. Another method for

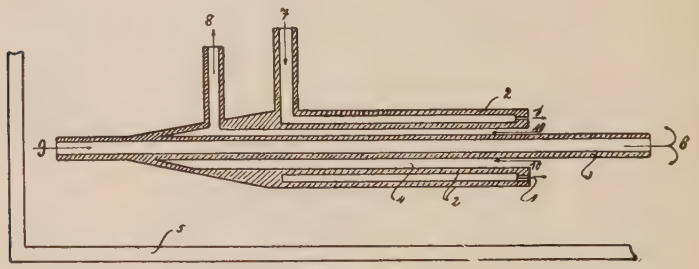


Fig. 97. Mönkemeyer's Apparatus for Spinning Hollow Threads

producing tubular artificial threads is described by Vereinigten Glanzstoffabriken, Elberfeld, in German patent 369,560. According to this patent, narrow bands, produced in the well-known manner by slits of any form, are twisted spirally to form a tube, either directly after spinning, or later after being once more bathed in liquid. This is proposed to be effected, for example, in a very simple manner by winding ribbon-shaped threads in a spinning centrifuge, whereby, as explained on page 79, they are twisted spirally. It is stated that interesting and technically valuable light effects are thus obtained in the hollow threads, for example, by the fact that several such bands are superposed. This can also be applied to other threads or bundles of threads which act as a core. The threads produced in this manner are to be used as artificial straw, artificial hemp, or artificial tagal fibre.

Processes for the manufacture of hollow threads by the production of gas bubbles within the thread have been described, for example, by L. Drut in German Patent 346,830, and by J. Rousset in German patent 370,471. The threads are obtained by spinning a solution which is either emulsified with an inert gas or in which the gas is dissolved under pressure, and immediately escapes in the form of bubbles when the solution leaves the spinning nozzle. A material may also be added to the spinning solution which develops gas in the precipitating bath on leaving the spinning nozzle. The gas bubbles cause a tension of the surface of the thread, which imparts a certain stiffness to the product and

reduces the flexibility and elasticity of the thread. The last-named inventor proposes to remove this disadvantage, according to German patent 378,711, by allowing the tubular structure to collapse to any required extent by removing the enclosed gas wholly or partially by treatment with a reagent which condenses, dissolves, or absorbs the gas, for example, by passing the thread into de-aerated water into which the gas diffuses.

CHAPTER XVIII

SHORT STAPLE ARTIFICIAL SILK PRODUCTS (IMITATION SCHAPPES, ARTIFICIAL COTTON, STAPLE FIBRE, ETC.)

THE artificial silk products which we have so far described consisted of continuously-spun threads of indefinite length. We have now to describe short-staple products of the artificial silk industry.

The natural textile fibres, with the exception of silk, are relatively short. The fibre length is described as the "staple"; the fibres are, therefore, described as "long staple" or "short staple" cotton, and so forth. In order to produce a long thread suitable for weaving, such short staple material must first be spun in the well-known manner. All such fibres, with the exception of silk, could therefore be described as "staple fibres," although this name is not usual. It is only used for such artificial silk fibres as are obtained by cutting long threads into short pieces of about the length of a cotton or wool fibre. We know, of course, that artificial silk, like natural silk, is produced in threads of practically unlimited length, only limited by the conditions of the manufacturing processes, and is therefore not a staple fibre, and requires no further spinning process for the production of a continuous thread suitable for weaving.

When, during the war, a serious shortage of cotton, wool, and so forth, occurred, more particularly in Central Europe, men's minds were naturally turned to the production of artificial threads in a form similar to that of these natural fibres, and therefore, of a similar staple, which could then be spun in a similar manner to cotton or wool, or further treated so that they might to some extent replace the natural products. These efforts succeeded on a very wide scale and in a comparatively simple manner, by cutting the artificial silk threads produced in the usual way, into short pieces of about the length

of a cotton or wool staple, that is, of about 3 to 6 cm. The products so obtained, which could be further treated in a similar manner to cotton or wool, were called " staple fibres."

Schappe Imitations, Artificial Cotton, etc. Forerunners of staple fibre had already been produced. If we remember that the characteristic of staple fibre is that it has first to be spun into a long thread suitable for weaving, similarly to cotton or wool, we will at once appreciate the derivation of the various products which were marketed as " artificial cotton," " imitation schappe," and so forth. The manufacture of these products developed from an endeavour to use the waste obtained in spinning and further treating artificial silk. This waste, after cleaning, constituted a loose, tangled mass of fibre similar to cotton wool, but even at the commencement of the century was usually mixed with other fibres, carded, combed, and spun like cotton, and so forth, on ring or flyer spinning frames. The increasing demand for these products, obtained from artificial silk waste, led to the idea of producing similar tangled masses of fibre deliberately in an artificial manner. It is easy to understand that the production of such material was simpler and cheaper than the manufacture of normal artificial silk, as it did not require such great care in order to produce a long, uniform, carefully-wound thread, free from air bubbles and entirely strong and resistant.

The first patented process of this kind is that described by Mitchel in British patent 29,030. In France, A. Pellerin was the first to propose the manufacture of such products on an industrial scale. According to the process described in his French patent 410,776, Austrian patent 55,749, Swiss patent 54,646, and U.S. patent 1,128,624, the viscose spinning solution is passed through a filtering material containing a large number of extremely small apertures ; for example, it is pressed through a fabric into a precipitating bath which may suitably consist of dilute sulphuric acid ; in this manner an irregular tangle of fibre, of the character above described, is produced. However, this process does not appear to have succeeded in practice, as the inventor proposes another method in his later patent, British patent, 7562/1913, German patent 271,215, French patent 442,022, Swiss patent 64,190, Belgian patent 255,192 and U.S. patent 1,184,206. According to this patent he proposes to inject the cellulose solution into the precipitating bath through perforated sieve plates which are arranged in several whorls round the walls of a tube through which the precipitating liquid is passed. The finely-perforated plates are arranged obliquely round the

tube, on a suitable support, in such a manner that a large number of threads are precipitated simultaneously by the same current of precipitating liquid. In his later British patent 121,734, German patent 370,444, French patent 466,292, and Swiss patent 41,746, Pellerin returns to the nozzle form by attaching capillary nozzles in the usual manner to the end of the spinning tubes, which, however, are so large and provided with so many spinning apertures, that by uniting the fibres from several nozzles several thousand fibres are present per metre of width. For removing the fibre he uses a revolving drum, the velocity of which can be varied at will ; the fibre mass is not, however, wound round this drum, but is detached from it by a scraper which passes it on to a collecting vessel. Bourbon and Cassier, in French patent 429,679, and A. Bloch in French patent 447,068, propose to introduce the cellulose solution into a centrifuge, the cage of which is provided with a large number of very fine openings. On revolving the centrifuge the spinning solution is forced into the coagulating bath in the form of very fine streams which are there coagulated in the form of very fine carded cotton. According to German patent 317,181, L. Fessmann proposes to produce similar masses of fibre by arranging two or more nozzles in opposition to one another, in such a manner that the streams of spinning solution expelled from these meet immediately beyond the nozzle apertures and are there distributed in tangled masses ; or by baffle planes of glass or metal in front of the nozzles which also cause tangled distribution of the spun product.

The strong lustre of artificial silk threads is, of course, not always desired in threads to be used as a substitute for cotton. In the General Section of this work we discussed the influence which the tension of the thread exerts on the lustre of the fibre during further treatment, more particularly during dyeing. As stated by Glanzfäden, A.-G., Petersdorf, in their German patent 312,304 and Swiss patent 84,238, which deal with the production of substitutes for cotton or wool, the tension of the fibre, whilst the chemicals which they contain are being removed by washing, has much effect on the lustre. If they are washed without any tension a dull and brittle product is produced. It was found that a firm thread with a gentle, wool-like lustre was obtained by the slight tension which is caused by pouring strong baths over the hanks, by which means there is no possibility of producing too strong a tension and so obtaining a product of the aspect of silk. The same firm attempts to achieve this purpose, that is, the formation of a strong and supple thread with a soft, woolly lustre, according to German patent 389,394. According to this patent it has been

found that a suitable product, witb the above-mentioned properties, is obtained from viscose solutions by hydrating the cellulose with caustic alkali to such an extent only that the xanthate obtained with carbon disulphide is barely completely soluble, and then spinning the viscose into dilute mineral acid, for example, 12 to 15 per cent sulphuric acid, without ripening.

Staple Fibre. This product has already been defined above (page 389), and is merely an artificial silk cut into small pieces. It does not, therefore, differ essentially from the products, also consisting of short fibres, which were described in the previous section. Staple fibre is only distinguished from them by the fact that the threads are cut fairly uniformly to a definite length, corresponding to that of cotton or wool fibres.

Since natural fibres have once more been obtainable in sufficient quantity, the importance of staple fibre has decreased, more particularly for worsted spinning, for which it was of the chief importance. It is, however, by no means impossible that new processes, which would increase its value as a substitute, might once more cause it to be more widely used.

P. Girard was the first to describe a process for the production of a similar product in 1912. According to his British patent 5386/1912, German patent 266,140, French patent 438,131, and patent of addition 15,399, Belgian patent 243,409 and U.S. patent 1,164,084, artificial fibres spun in the usual manner are wound in parallel layers on to spools or reels and are then cut one or more times, in parallel to the axis of the spool, in order to convert the thread into a collection of short fibres of equal length, lying parallel to one another. A process which scarcely differs from that of Girard is described by P. Vindrier in French patent 442,015, which was exploited by the Soc. Franco-Suisse des Textiles Chimiques after patent litigation with the Viscose Group had been settled.

L. Fessmann proposes to avoid the necessity for winding and subsequent cutting, by producing short lengths of fibre immediately on spinning. According to his German patent 319,079 this aim is achieved by interrupting the squirting process at definite intervals. The same purpose is attempted in his German patent 319,280, according to which the squirted thread is torn away from the nozzle after it has reached a definite length. It is stated that the ends of the fibres are thus drawn out to points.

In practice, it has been universally found that the Girard process of cutting the threads on the spools or reels is the most practical.

In German patent 343,723, E. Schülke has described an apparatus for the production of staple fibre, according to which the threads pass from the spinning bath over rollers with an elastic surface and a belt

conveyor into a slowly revolving centrifuge, in which, after they have accumulated sufficiently, they are freed from the spinning bath by increasing the rate of revolution, and further treated, that is, washed and so forth. The patent of addition 343,753 contains certain improvements of the process. More particularly, a pair of rollers is provided, which simultaneously receive bundles of fibres coming from two opposed directions, that is, from opposed sets of spinning nozzles. A second patent of addition, German patent 381,669 of the Sudenburger Maschinenfabrik und Eisengiesserei A.-G., describes special improvements of the centrifuge serving to collect the threads, particularly the insertion of a contrivance which ensures the uniform deposition of the fibres which are introduced, which are deposited between this latter and the cage.

In order to render staple fibre and similar fibrous material suitable for the subsequent combing and spinning processes, it is of advantage, according to German patent 382,467 of the Köln-Rottweil A.-G., to treat it with dilute aqueous solutions of the lower fatty acids (for example, with ½ per cent acetic acid), instead of with the usual soap bath only.

In German patent 319,839, L. Meyer proposes to produce a crimped effect on staple fibre, similar to that on wool, by rapidly heating or cooling the fibre. Heating may be carried out, for example, by high pressure steam ; the degree of crimping is said to depend on the degree of temperature applied, and very rapid cooling is said to have a similar effect. It is stated that the crimped fibre can be spun particularly well and with a higher yield, as in consequence of the improved adhesion less waste is produced. It is stated that the yarns obtained from crimped staple fibre are very open and loose, and similar to those obtained from wool. According to H. Voss's German patent 363,379, a good crimping effect is obtained by spreading the cut fibre to a loose mass and then fixing it whilst free from tension.

A whole number of uses for staple fibre have been found, but they have diminished in importance during the last few years. The product has been found to be satisfactory in weaving, particularly when admixed with wool, with which better results are obtained than when admixed with cotton. It is found to be best not to use threads separately produced from wool fibre and staple fibre, but mixed threads spun from wool and from staple fibre together. From 30 to 50 per cent. and even more, of staple fibre is mixed with the wool. It was found that shoddy could be worked up comparatively satisfactorily together with staple fibre.

Staple fibre may also be spun together with cotton and silk, but finds less application in this form than when spun with wool. Such products are used together with pure cotton or silk threads in the weft or the warp or as fancy threads.

It should be mentioned that staple fibre is said to have been found suitable for the manufacture of gas mantles in place of ramie fibre or ordinary artificial silk.

Threads Cut from Films. Another method of producing more or less short staple artificial threads must be mentioned, which has not attained any considerable technical importance hitherto, and does not appear likely to do so in the future. It arose out of the necessities of the war and post-war period, and consisted in first producing the cellulosic material in the form of wide ribbons or sheets and then cutting these into very narrow thread-like strips which could then be spun into long threads in a similar manner to the staple fibres described in the previous pages. However finely these threads may be cut, they naturally always differ from the threads obtained from round nozzle apertures by the fact that they have sharp edges. Otherwise they are straight and stiff, and therefore show but little elasticity, although a certain degree of this quality may be imparted to them by special methods, for example, by crimping.

Thus, in German patent 302,611/1917, P. Krais describes a process for the production of wool-like artificial fibres and threads, thereby characterized that films are produced from very finely-ground woollen, hair, horn, or leather waste and suitable binding materials, these films being then cut into fibres which are spun either alone or in admixture with other fibres. The following are mentioned as suitable binders: gelatin, glue, acetyl-cellulose, or other viscous solutions of cellulose or cellulose compounds, with the addition of materials to impart flexibility. It is stated that gelatin or glue must subsequently be rendered waterproof by the action of formaldehyde, tannin, or the like. According to patent of addition 303,731, paper pulp is used as a binding material and is subsequently parchmentized. We must refer here to German patent 349,461 of E. Claviez, which is described in the next section. According to German patent 318,741 of H. Freise, such cut products are rendered more elastic by crimping, which effect can easily be achieved by producing small ridges in the strips of film in a longitudinal direction, for example, by passing them between corrugated rollers before finally hardening. On cutting the films, crimped, springy fibres are then obtained, similar to wool fibres.

THREADS FROM MIXTURES OF ARTIFICIAL AND NATURAL FIBRES

Threads of artificial silk material containing an internal core of one or more natural threads have already been referred to.

Threads have, however, also been produced containing more or less considerable quantities of natural fibre dispersed throughout their substance. According to their inventor, E. Claviez, such threads are distinguished by great strength and can be used for very many purposes. They are prepared by spinning cellulose solutions of all kinds with which vegetable or animal fibres have been incorporated. The finished threads are said to contain the natural fibres in unaltered or but slightly altered form. The diameter of the nozzle apertures must naturally be sufficiently wide, so that the admixed fibres may pass through unhindered together with the cellulose solution. The desired fineness of the thread is then attained by subsequent stretching.

According to German patent 349,461 of the same inventor, cut threads of a similar character can be obtained by producing wide bands or sheets from cellulose solutions mixed with textile fibres of any kind, such bands or sheets being then cut in the above-described manner.

IMITATION TEXTILES

Not only have threads for weaving and other purposes been produced from cellulose solutions and also from gelatin and casein solutions and so forth, but finished textile products have also been imitated by converting the spinning solutions into films, which are then perforated in a regular manner in order to produce a homogeneous, uniform mass roughly resembling in shape a textile structure. These cannot be described as "textiles," but as "imitation textiles," as no individual threads are present, but are merely imitated by the nature of the design. In this manner imitations of gauze, muslin, and similar fabrics and also of lace and embroidery have been produced, which cannot, of course, in the least replace the real products, being much inferior to these in tenacity, handle, resistance to water, and other properties. They are, therefore, only suitable for subordinate uses.

The manufacture of such products is usually carried out by pouring the spinning solution on to a slowly-rotating roller, the surface of which is engraved with a pattern corresponding

to that of the textile to be imitated. Excess of spinning solution is removed by a doctor, in a similar manner to the paste during calico printing, and the thin layer of spinning solution remaining on the roller is coagulated by a suitable liquid in a manner similar to that used in spinning artificial silk, so that the film which is produced retains the pattern engraved on the roller. The precipitating bath is either sprayed on to the roller covered with the cellulose solution, or the lower portion of the roller itself dips into the precipitation bath.

Processes and contrivances of the above-mentioned kind are described in Austrian patent 138, German patent 200,509, French patents 368,393 and 384,751 ; also by M. Ratignier and the Société H. Pervilhac & Co., in British patent 13,518/1907, German patent 200,509, Austrian patent 33,498, Swiss patent 40,674 and French patent 384,934 ; by de Sauverzac in French patent 420,086 ; by the Cie Française des Applications de la Cellulose in British patent 5077/1911, Austrian patent 58,795, and U.S. patent 995,652 ; by Schmid & Co. and J. Foltzer in Swiss patents 69,514 and 70,719, and by R. Borzykowski in French patent 461,400.

CHAPTER XIX

ECONOMICS AND STATISTICS

We wish to state in advance that it is very difficult to obtain reliable figures regarding the artificial silk industry, and that those obtained from various sources often vary considerably. In the following tables, where it appeared desirable, figures from other sources which differed considerably have been appended in brackets. The figures below have been obtained from the best possible sources, but the absolute correctness of all the figures cannot be guaranteed. With this reservation, the following figures may now be given.

WORLD PRODUCTION

A general picture of the enormous development of the artificial silk industry and the rapidity with which this development has occurred—particularly during the last ten years—is given by the following table, which shows the production of artificial silk during several years—

Year	World production in tons	Year	World production in tons
1896	600	1921	20,000
1907	2,900	1922	36,121
1909	5,000	1923	44,200
1913	9,000	1924	62,797
1916	13,500	1925[1]	70,000
1920	18,000		

The following figures show how the world production of natural silk developed during the same period—

Year	World production in tons	Year	World production in tons
1904	21,145	1922	32,500
1909	24,500	1923	30,460 (34,000)
1912	26,770	1924	about 32,000
1913-14	27,320		

[1] Estimated from figures for first half of year.

Thus, in 1922, the production of artificial silk already exceeded that of natural silk, and is now about two-fold the production of the latter.

RELATIVE OUTPUTS OF THE VARIOUS PROCESSES

It is interesting to compare the relative proportions of the output of artificial silk, both formerly and to-day. According to F. Becker (*loc. cit.*, page 348), the total production of artificial silk, of about 5,000,000 kg. in 1909, was distributed between the various processes as follows—

		kg.	kg.
Collodium Silk	Besançon	800,000	
	Tubize	800,000	
	Frankfurt a. M.	800,000	
			2,400,000
Cuprammonium Silk	Elberfeld	1,000,000	
	Givet and Izieux	300,000	
	St. Pölten	500,000	
			1,800,000
Viscose Silk	Sydowsaue	100,000	
	Arques la Bataille	100,000	
	Courtauld & Co.	500,000	
	Belgium (Ruysbroeck and Alost)	100,000	
			800,000
			5,000,000 kg.

The figures and percentages for the various processes in 1909 and 1924 are shown in the following table—

	1909	1924
Collodium silk	2,400,000 kg. = 48%	4,900,000 kg. = 7·8%
Cuprammonium silk	1,800,000 kg. = 36%	900,000 kg. = 1·4%
Viscose silk	800,000 kg. = 16%	55,190,000 kg. = 88·0%
Acetate silk	—	1,800,000 kg. = 2·8%

It will be seen that the production by the Chardonnet process, which amounted to almost one-half of the total artificial silk production in 1909, now amounts to 7·8 per cent only, although the production of collodium silk is now almost double that in 1909. The relatively expensive cuprammonium process has receded still more in relative importance, which

may be explained by the fact that cuprammonium silk is mainly preferred for certain definite articles only, but has otherwise been replaced by the cheaper viscose silk, which for the present monopolizes the lion's share of the market. Cuprammonium silk has even been over-reached by acetate silk, which already represents an appreciable proportion of the total production, as will be seen from the table.

PRODUCTION ACCORDING TO COUNTRIES

The following table shows how the production of artificial silk during the last few years is distributed in the various countries.

For 1924 percentages of the world's output produced by the various countries have also been added. In the last column estimates have been given of the production during 1925, but these naturally have no pretensions to accuracy.

	1922 Tons	1923 Tons	1924 Tons	1924 Per cent	1925 Tons (estimated)
U.S.A.	10,645	14,000	16,245 (22,000)	25·87	22,650
England	6,940	7,000	10,885 (6,300)	17·33	6,342 (7,300)[1]
Germany	5,700	6,000 (7,000)	10,760 (9,000)	17·13	9,060 ?
Italy	2,850	4,600	8,400 (12,600)	13·38	12,684
France	2,850	3,500	5,606 (6,300)	8·93	6,342
Belgium	2,850	2,800	4,034	6·42	4,077
Switzerland	855	1,700 (2,500)	1,820 (2,700)	2·90	2,718
Holland	1,140	1,200	1,530 (3,200)	2·44	3,171
Austria	712		1,200	1·91	906
Hungary	855	3,200	280	0·45	453
Poland	427	450	700	1·11	453
Czecho-Slovakia	285		588	0·94	680
Spain			84	0·13	136
Japan	112	200	545	0·87	?
Sweden			80	0·13	?
Russia			40	0·06	?

[1] According to the English Press these figures for English production are greatly under-estimated.

Thus, America is by far the largest producer. It is interesting to note the development of the output of that country during the last ten years, which was as follows, in millions of kilograms—

1913	1914	1915	1916	1919	1920	1921	1922	1923	1924	1925
0·71	1·11	1·86	2·6	3·7	4·6	6·8	10·6	14·0	16·2	22·6

It may also be noted from the above table that in 1925 Italy attained the second place and thus exceeded England and Germany in output. It should also be noted that if the estimates are correct Holland passed Switzerland in the race.

EXPORTS, IMPORTS, AND CONSUMPTION

It would take too much space to give the figures under these headings for all the states over several years. We will, therefore, select the more interesting figures.

GERMANY. In the years 1920 to 1923 Germany imported and exported the following quantities—

	1920	1921	1922	1923
Imports (tons) . .	257	794	1271	268
Exports „ . .	242	227	998	1556

From these figures it follows that in 1922, with a production of 5700 tons, the internal consumption was 5973 tons, and in 1923, with a production of 6000 tons, the internal consumption was 4712 tons.

According to *Commerce Monthly*, New York, 1925, No. 1, page 27, the imports and exports of Germany in 1924 were 2,394,857 lb., and 5,176,180 lb. respectively, the excess of exports being thus 2,781,323 lb.

SWITZERLAND. The following statistical figures have been published—

	1920	1921	1922	1923	1924 (till Sept.)
Imports (tons) .	494	374	886	956	1038
Exports „ .	385	837	820	628	695

From the figures for 1922 and 1923, together with the production in those years, already given, it follows that the domestic consumption in 1922 and 1923 was 921 and 2028 tons respectively.

France. This country imported considerably more artificial silk than it exported. In 1923 the exports are stated to be 220 tons and the imports 775 tons, so that the domestic consumption was 4055 tons. The corresponding figures for 1924 were—

Imports	1,753 tons
Exports	138 „
Consumption (for a production of 5,606 tons)	7,615 „

Italy. For the years 1920 to 1923 the statistics were as follows—

	1920	1921	1922	1923
Imports (tons) . .	374	305	433	547
Exports „ . .	406	1050	2006	2736

For 1922 and 1923 the figures show a domestic consumption of 2411 tons.

According to *Commerce Monthly* (*loc. cit.*), in 1924, the imports were 1,339,158 lb. and the exports 9,986,373 lb., showing an excess of exports of 8,647,215 lb.

England. In 1924 the imports were 10,281,668 lb. and the exports 6,350,905 lb., showing an excess of imports of 3,930,763 lb. The value of this excess of imports is said to have been £556,358, whilst the corresponding value for 1923 was £563,458.

U.S.A. The imports of the United States consist mainly for the present of artificial silk waste. The total imports in 1923 were 3130 tons, 43 per cent of which was waste, and in 1924, 3215 tons, of which 76 per cent was waste.

According to *Commerce Monthly* (*loc. cit.*), the imports of U.S.A. in 1924 were 1,711,987 lb., and the exports only 559,479 lb., showing an excess of imports of 1,152,508 lb.

Japan. This country imported considerable quantities of

artificial silk, but the imports in 1924 were considerably less than those of the preceding year. The statistics are as follows—

	1913	1920	1922	1923	1924
Imports (in tons) .	76·8	36·3	101	457	275

FIRMS AND WORKS

The number of artificial silk works was 22 in 1906 and 95 in 1924. These belonged to 79 various firms, of which the most important are as follows—

GERMANY. Vereinigte Glanzstoffabriken A.G., Elberfeld (works at Oberbruch), (this firm owns the staple fibre works Jordan & Co., Sydowsaue, and the Bayerische Glanzstoffabrik A.G., Obernburg); Vereinigte Kunstseidenfabriken A.G., Kelsterbach; Glanzfäden A.G., Berlin (works at Petersdorf); Köln-Rottweil A.G., Berlin, with works at Rottweil, Premnitz, Bobingen, Eilenburg; J. P. Bemberg A.G., Barmen; Fr. Küttner, Pirna; Aktiengesellschaft für Anilinfabrikation, Berlin (works at Wolfen); Dynamit A.G., vorm. A. Nobel & Co., Hamburg (Konzern Köln-Rottweil); Zellstoffverwertungs A.G., Pirna; Hölkenseide G.m.b.H., Barmen; Spinnstoffabrik Zehlendorf G.m.b.H., Berlin; Borvisk Kunstseiden A.G., Herzberg i. Harz; Spinnfaser A.G., Elsterberg i. V.; Herminghaus & Co., Vohwinkel; Kunstseidenspinnerei Mez, Vater & Söhne, Bräunlingen; Spinnstoffwerk Glauchau A.G., Glauchau; Viscose A.G., Arnstadt i. Thür.; Monitwerke G.m.b.H., Heidenau; Neue Baumwollspinnerei, Bayreuth; Kunstseidefabrik Schwetzingen (Rhein. Gummi- und Cellulosefabrik); Paverin A.G., Charlottenburg; Kunstseidenspinnerei Münchenbernsdorf; Georg von Giesches Erben, Chem. Textilwerke, Breslau.

SWITZERLAND. Société de la Viscose Suisse, Emmenbrücke (works at Emmenbrücke and Heerbrugg); Kunstseidefabrik Arbon; Borvisk Kunstseidenwerke A.G., Zürich (works at Steckborn); Stickerei Feldmühle A.G., Rorschach; Spinnerei Rheinfelden A.G.; Schonlau & Co., Riehen; Technochemica A.G., Glarus.

FRANCE. Société anonyme pour la fabrication de la Soie de Chardonnet, Besançon; Société pour la fabrication de la Soie "Rhodiaséta," Paris; Société Chimique des Usines du Rhône (works at Saint-Fous); La Soyeuse Française, Paris (Rantigny); La Soie d'Argenteuil; Société Lyonnaise de Soie artificielle, Decines; La Soie de Valence, Allegre & Mondon, Valence; Meunier & Cie, Neuville, s/Saône; Société anonyme des Textiles Synthétiques, Terre-Neuve près Montluçon; Société Borvisc, Paris (works at Nièvre); La Soie Artificielle Française, Paris (Rennes).

BELGIUM. Société Générale de Soie Artificielle par le procédé Viscose, S.A. Alost (Flanders); Société Anversoise de Soie Artificielle (works at Schooten); Textiles Belges, Obourg-les-mons; "La Seta," Fabrique

de Soie Artificielle, S.A. Brussels; Fabrique de Soie Artificielle de Tubize; Société anonyme des Soieries de Maransart.

England. Samuel Courtauld & Co, Ltd., London (works at Coventry and Wolverhampton); British Cellulose and Chemical Manufacturing Co. Ltd., London (now British Celanese, Ltd.); Boroid, Ltd., London; British Cellulose Syndicate, Ltd., London; United Celluloid Silk Spinners, Ltd., Yarmouth; Yorkshire Artificial Silk Co., Ltd.; Peter Spence & Sons, Ltd., Manchester; Twyer Co., Bury (works at Gloucester); Brysilka Co., Apperley Bridge; Harbens, Ltd., Golborn (Lancashire); Kent Silk Mills, Sidcup; Lustrafil, Ltd., Nelson; The Palatine Artificial Yarn Co., Ltd., Manchester.

Italy. Società Nazionale Industria Applicazioni Viscosa (abbreviated to "Snia-Viscosa"), Turin (works at Pavia, Veneria Reale and Cesano Maderno); Società anonima di Seta Artificiale, Milano (works at Varedo and Ceriano); Società anonima di Manifattura Seta Artificiale, Milan; Società anonima Seta Artificiale Cremona (Pizzighettone); Società anonima Viscosa Vercellese; Societé anonyme La Soie de Chatillon.

U.S.A. Viscose Co., Marcus Hook (Pennsylvania); Belamose Corporation, Rockey Hill (Conn.); Du Pont Fibre Silk Co., Buffalo (N.Y.); Industrial Fibre Co., Cleveland (Ohio); Tubize Artificial Silk Co., Hopewell (Va.); Cupra Inc., Athenia (New Jersey); American Cellulose and Chemical Co., Cumberland (Maryland); Lustron Co., Boston (Mass); Artificial Silk Co. of America, Philadelphia (works at Camdon, N.Y.); National Artificial Silk Co., Cleveland; Otto B. Shulhof & Co., New York; The Acne Artificial Silk Co., Cleveland (Ohio); Genasco Silk Works, Landsdowne.

Holland. Nederland'sche Kunstzyde-Fabrik, Arnhem and Ede; N. V. Hollandsche Kunstzyde-Industrie, Breda.

Austria. Erste Österreichische Glanzstoffabrik, A.G., St. Pölten.

Hungary. Magyar Chardonnet Selemgyar, Sárvár; Kunstseidefabrik A.G., Ungarisch-Altenburg (Magyarovar).

Czecho-Slovakia. Böhmische Glanzstoff-Fabrik (System Elberfeld), Lobositz; Erste Böhmische Kunstseidefabrik A.G., Theresienthal bei Arnau; Kunstfaserfabrik A.G. at Senica.

Russia. Russische Viscosegesellschaft (Mitischtschi Works); Société anonyme pour la Fabrication de Soie Artificielle, Moscow.

Poland. Kunstseiden-Aktiengesellschaft Tomaszow, near Lodz; Société anonyme des Soieries de Sakhatschew, Bariszew; Goldammer & Eck, Lodz.

Sweden. Aktiebolaget Svensk Konstsilke, Boras.

Canada. Courtaulds, Ltd. (London), works at Cornwall (Ontario).

Brazil. Kunstseidenfabrik Rio de Janeiro.

Japan. Asahi Jinzo Kenshoku A.G. (works at Zeze); Celluloid and Artificial Silk Co., Aboshi, near Himeji; Fuji Jinzo Kenshi A.G., Zeze; Japan Artificial Silk Co., T. Watanabe (Mogi & Co., New York) (works at Kogasu, near Yokohama, and at Mie); Kawagoye Jinzo Kenshi works at Kawagoye); Nippon Jinzo Kenshi (two works at Tsurumi and Tsu); Teikoku Jinzo Kenshi (works at Yonezawa and Hiroshima.) Tokio Jinzo Kenshi Seizosho at Matsuda. Toyo Jinzo Kenshi Matsuzaka. Sakai Celluloid Co.

ARTIFICIAL SILK PRICES

In 1924 the average price of artificial silk was 23 to 27 marks per kilogram (10s. 5d. to 12s. 3d. per lb.). At the end of 1906 this price had fallen to 15 marks per kilogram (6s. 10d. per lb.). In 1914 in Germany the average price for both imports and exports was 12 marks per kilogram (5s. 5d. per lb.), whilst real silk at that time cost 40 marks per kilogram (18s. 1d. per lb.).

To-day, the average price for goods of first quality is 16 to 20 marks (7s. 3d. to 9s. 1d. per lb.), and for second quality 11 to 14 marks per kilogram (5s. to 6s. 4d. per lb.). The fine counts are naturally considerably dearer than the coarser counts. For the finer qualities the price to-day is about half that of real silk, and for poorer qualities only about one-third the price. The price of the finest counts (50 deniers) is about double that for the coarser counts (450 deniers).

At present wages are the dominant factor in the production cost, and according to a communication in *Die Kunstseide*, 1925, p. 42, it is now possible in Italy, where the wages are relatively low, to produce viscose silk yarn at a price of about 2s. per lb.

Finally, we append a table giving the prices quoted by American works in March, 1925, in dollars per pound.

Deniers	1st quality	2nd quality	3rd quality
50	3·50	—	—
60	3·40	3·15	2·50
70	3·25	3·05	2·50
75	3·10	2·90	2·70 (?)
80	3·10	2·90	2·40
90	3·00	2·80	2·50 (?)
100	2·90	2·70	2·30
120	2·45	2·30	2·10
130	2·25	2·10	1·90
140	2·15	2·00	1·85
150	2·00	1·90	1·80
160	2·00	1·90	—
170	1·90	1·80	—
180	1·90	1·80	—
200	1·90	1·80	1·70
300	1·75	1·65	1·55
450	1·75	1·60	1·45

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